THE DISTRIBUTION OF SILICON BETWEEN LIQUID SLAG AND IRON

T H E S I S

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1. INTRODUCTION

The control of silicon is an important problem in all blast furnace operations and particularly so in the case of irons to be used in steel manufacture. It is desirable that the silicon content of such irons should be kept as low as possible because of the increased slag volume which an increase of silicon in the hot metal entails. In the case of foundry irons it is again desirable that the silicon content can be controlled within comparatively narrow limits because of the major influence of silicon on graphitisation which in turn controls the mechanical properties of the final casting,

There is little doubt that the temperature of the blast furnace hearth is one of the major factors controlling the silicon content of pig iron; high temperatures being one of the prerequisites for high silicon iron whereas low silicon contents are obtained with low hearth temperatures.

The control of silicon becomes more difficult, however, when the question of sulphur removal is also considered. Hearth temperature is also one of the factors controlling the sulphur content of pig iron; other factors being equal, the higher the hearth temperature the lower the sulphur content of the pig iron.

It is thus seen that the hearth temperature cannot be varied indiscriminately. A compromise must be struck which will keep the silicon content within the desired range and yet will give the required degree of desulphurisation.

Another factor in the control of both sulphur and silicon is that

of slag basicity. The more basic the slag the greater is the degree of desulphurisation and the lower is the silicon content of the pig iron. Here again, however, the slag composition can only be varied within narrow limits because of the increased melting point and viscosity of slags of higher basicity.

It can be shown theoretically, and has been shown experimentally in the case of sulphur[1], that the oxidising power or "oxygen potential" of the slag also has a major influence on the equilibrium silicon and sulphur content of the underlying metal. Other factors being equal, an increase in the oxygen potential of the slag results in a decrease in the silicon content and an increase in the sulphur content of the metal.

The reactions occurring in the hearth of the blast furnace can be divided into two categories. There are firstly the reactions taking place between slag and metal and secondly those taking place between the slag and the solid carbon present in the form of coke. If equilibrium were attained in the furnace then the FeO content of the slag would be controlled by the reaction

$$(1)\quad (FeO) + C_{sol.} = \underline{Fe} + CO.$$

where bracketting and underlining denotes solution in slag and metal respectively. The silicon and sulphur would be distributed according to the reactions

$$(2)\quad 2(FeO) + \underline{Si} = \underline{2Fe} + (SiO_2)$$

$$(3)\quad (FeO) + (CaS) = \underline{FeS} + (CaO)$$

or, as the FeO is in equilibrium with solid carbon, according to the reactions

$$(4)\quad (SiO_2) + 2C_{sol} = \underline{Si} + 2CO$$

$$(5)\quad \underline{FeS} + (CaO) + C_{sol} = \underline{Fe} + (CaS) + CO$$

There is little doubt, however, that reaction (1) does not come to equilibrium in the blast furnace. It has been found [2] in laboratory studies that the FeO content of blast furnace type slags in equilibrium with solid carbon at 1500°C is of the order of 0.05%, much less that the $\frac{1}{2}$ to 1% which is the approximate amount normally found in blast furnace slags.

Laboratory studies [2, 3] of reactions (4) and (5) have shown further that the sulphur and silicon contents of blast furnace metal depart greatly from the equilibrium values. Whether or not this departure is due entirely to the non-equilibrium FeO content of the slag or partly due to this and partly to the non-attainment of equilibrium between slag and metal is, however, not known.

A study of reactions (4) and (5), although of much theoretical interest, is thus insufficient when considering the conditions present in the hearth of the blast furnace and for this reason the major aim of the present work was to investigate the effect of varying oxygen potentials of a blast furnace type slag on the silicon content of the metal. Other work[4] done concurrently was to study the effect of this variable on the sulphur distribution.

The oxygen potential was conveniently altered by varying the FeO content of the slag so that the reaction studied was

$$(2)\quad 2(FeO) + \underline{Si} = (SiO_2) + 2Fe$$

where the FeO and SiO_2 were dissolved in a lime-alumina-silica-ferrous oxide slag and the silicon in iron containing approximately 3% carbon. Beaause of the presence of this amount of carbon, the reaction

$$(6)\quad (FeO) + \underline{C} = \underline{Fe} + CO$$

could also be studied.

From known thermodynamic data, equilibrium constants for the above reactions can be calculated but such constants involve chemical activities and are of little practical use unless the relationships between activity and composition are known. Such relationships, have been determined for some of the reactants and resultants of the above reactions and from a comparision of experimental results with calculated constants it will be possible to obtain the activities of the other participating substances.

2. REVIEW OF LITERATURE.

Although a considerable amount of experimental work on the reactions

$$\underline{Si} + (2FeO) = (SiO_2) + \underline{2Fe}$$

and $$\underline{C} + (FeO) = CO + \underline{Fe}$$

has been published, the range of compositions investigated is more applicable to the steelmaking than to the blast furnace process. This is probably due to the difficulty in finding a crucible material suitable for holding blast furnace type slags containing FeO and also to the fact that steelmaking being a refining process in which the reactions require closer control has claimed more of the attention as regards slag-metal studies.

With regard to the reaction involving the reduction of silica by carbon from slags containing little or no FeO there is considerably more information.

Richardson and Jeffes[5] in a very comprehensive study collected the relative thermodynamic data and applied it to the blast furnace process. They developed the useful concept of "oxygen potentials". The oxygen potential of a system is defined as being equal to $RT \log_e p_{O_2}$ where p_{O_2} is the equilibrium partial pressure of oxygen of the system.

In a system in which pure metal and its oxide are in equilibrium we have

$$M + O_2 = MO_2$$

and $K_T = \frac{a_{MO_2}}{a_M{}^x p_{O_2}}$ where a_{MO_2} = activity of oxide

and a_M = activity of metal.

Assuming no mutual solubility of metal and oxide,

$$a_{MO_2} = a_M = 1$$

and $$\Delta G^o = -RT \log_e K_T = RT \log_e p_{O_2}$$

i.e. the oxygen potential of such a system is the same as the standard free energy change accompanying the formation of 1 gm mole of oxide from metal and oxygen at 1 atmosphere pressure. In this case an increase in oxygen potential would cause more oxide to form until the equilibrium partial pressure had been restored and conversely a decrease would cause the oxide to dissociate.

Considering the more general case where the activities can be other than unity which would be so when M and MO_2 were respectively dissolved in metal and slag solutions, we have

$$K_T = \frac{a_{MO2}}{a_M{}^x p_{O_2}}$$

and $$RT \log_e \frac{a_{MO_2}}{a_M} = RT \log_e p_{O_2} - \Delta G^o.$$

As ΔG^o is constant at any one temperature an increase in p_{O_2} causes an increase in the ratio $\frac{a_{MO_2}}{a_M}$ and vice versa.

Richardson and Jeffes consider that because of the presence of

solid carbon the partial pressure of oxygen in the hearth of the furnace is that in equilibrium with carbon and carbon monoxide at approximately 1 atmosphere partial pressure, i.e., the oxygen potential is the standard free energy change for the reaction

$$2C + O_2 = 2CO$$

at the particular temperature considered.

Making this assumption the authors have calculated the ratios of activity of oxide to activity of metal which would be expected for the various elements involved in the blast furnace process. As they point out, the difficulty is in translating these activity ratios into concentration ratios; little experimental data being available on the relationships between activities and concentrations. Their calculations are sufficient to show that for a given activity of silica in the slag an increase in temperature would cause an increase in the silicon content of the metal. Also that for the reaction

$$\underline{FeS} + (CaO) + C_{gr.} = Fe + (CaS) + CO$$

an increase in temperature causes an increase in the ratio $\frac{a_{CaS}}{a_{CaO} \times a_{FeS}}$.

i.e., for a constant activity of lime in the slag, sulphur passes from metal to slag with increasing temperature. Using that data which is available on the activities of silicon and sulphur in iron the authors consider that in actual blast furnace practice equilibrium is not

attained and that the contents of silicon and sulphur in the metal are respectively below and above the corresponding equilibrium values.

Because of the lack of stirring and the small contact area between metal and slag it is considered that little reaction takes place after the metal has been laid down; most of the reaction occurring as the metal droplets pass thrcugh the slag. Because of the displacement from equilibrium these droplets will be gaining silicon and losing sulphur during their passage through the slag. The authors point out that temperature, slag thickness and the compositions of slag and metal are varying continuously during the working of the furnace. Thus, it is not surprising that variations in metal composition during tapping are encountered. Because of the fact that silicon and sulphur contents usually flucuate in opposite directions, Richardson & Jeffes consider that the cause of these variations are slag thickness and temperature. Changes in the other variable which they discuss, slag basicity, would, of course, cause sulphur and silicon to decrease and, increase together.

A variable not discussed by the authors, the FeO content of the slag would, however, also cause silicon to vary in the opposite sense to the sulphur. Using the available thermodynamic data on the reactions

$$Si + O_2 = SiO_2$$

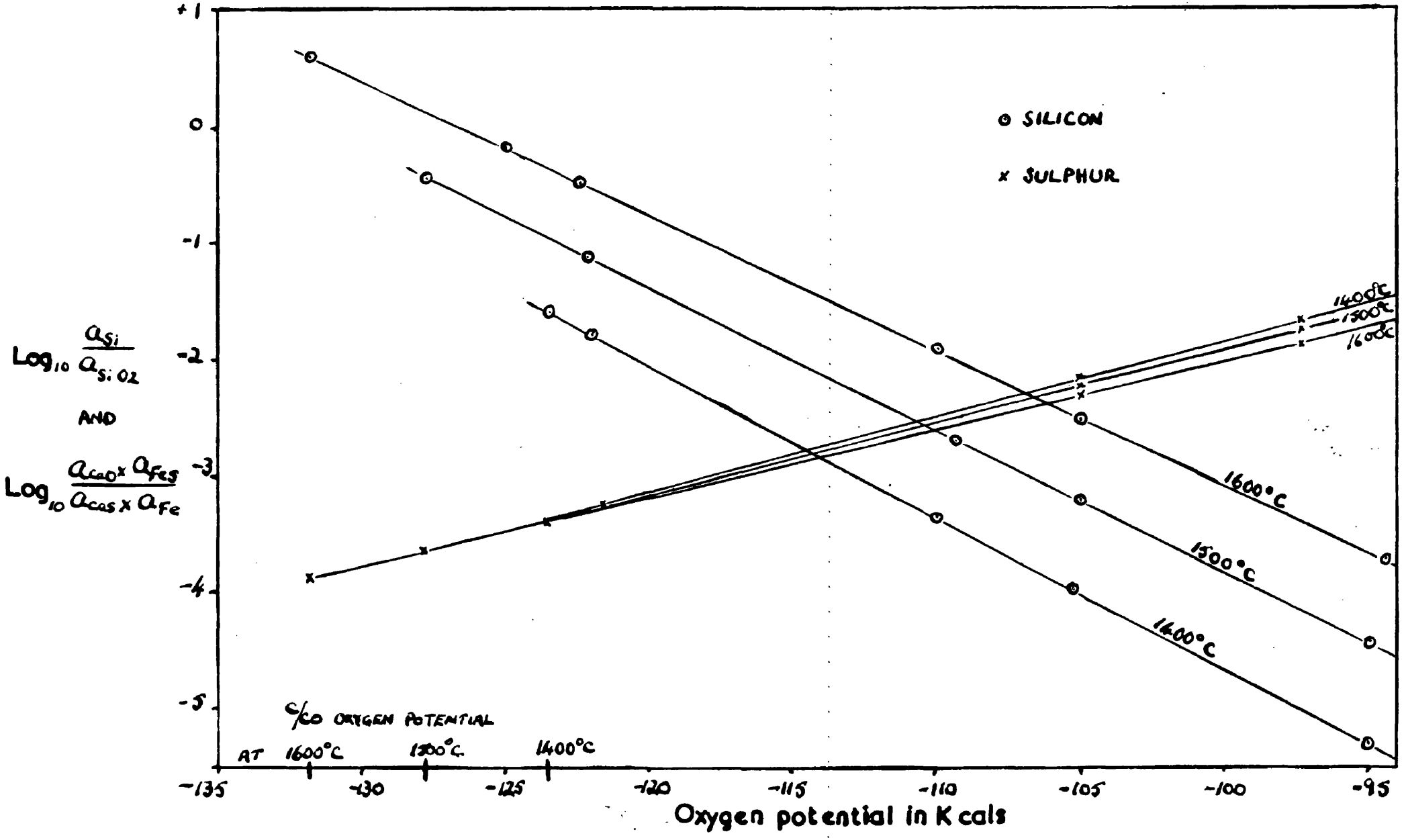
and

$$2CaS + 2Fe + O_2 = 2FeS + 2\ CaO$$

it is possible to calculate how the ratios $\frac{a_{Si}}{a_{SiO_2}}$ and $\frac{a_{FeS} \times a_{CaO}}{a_{CaS} \times a_{Fe}}$ vary with varying oxygen potentials. This has been done for the three temperatures 1400, 1500 and 1600°C and the results of the calculations are shown in Fig. (1). At each of the temperatures $\log \frac{a_{Si}}{a_{SiO_2}}$ decreases linearly with increasing oxygen potential and also for a given oxygen potential increase in temperature results in an increase in $\frac{a_{Si}}{a_{SiO_2}}$. Conversely the ratio $\frac{a_{FeS} \times a_{CaO}}{a_{CaS} \times a_{Fe}}$ increases with increasing oxygen potential and for a given oxygen potential decreases with increasing temperature. In this case however the change with temperature is small and is especially so at the lower oxygen potentials. Thus if silicon and sulphur contents of blast furnace metal vary in opposite directions it is more likely that the direct controlling factor is the oxygen potential of the slag rather than the temperature. It is highly probable however that one of the main factors in controlling the oxygen potential of the slag is the hearth temperature. Thus, not only will reaction

$$C_{gr.} + (FeO) = CO + Fe.$$

proceed faster at higher temperatures, but also the final equilibrium position will move to lower FeO contents; both of which factors will contribute to low FeO contents and thus lower oxygen potentials of the slag.



Fig(1) Variation of the calculated silicon and sulphur distributions with oxygen potential

Oelsen and Maetz[6] also recognised the importance of the oxygen potential or, as they called it, the degree of reduction of the slag, in determining the distribution of elements between slag and metal. They point out when considering the two reactions

$$(a) \quad (SiO_2) + 2C = \underline{Si} + 2CO$$

and $$(b) \quad (FeO) + C = \underline{Fe} + CO$$

that reaction (a) cannot go on indefinitely because of the possibility of the reaction

$$\underline{Si} + (2FeO) = (SiO_2) + 2Fe$$

taking place.

Similarly the sulphur transfer reaction,

$$\underline{FeS} + (CaO) + C = (CaS) + Fe + CO$$

and the reaction

$$(SiO_2) + 2C = \underline{Si} + 2CO$$

are linked by the reaction

$$2Fe + (2CaS) + (SiO_2) = \underline{Si} + \underline{2FeS} + 2(CaO)$$

The various reduction reactions thus mutually influence one another and the final equilibrium position of them all will depend on the oxygen potential of the system. The authors in considering a measure of the

oxygen potential consider, but reject, the FeO content of the slag. They argue that because of the small FeO content and the presence of iron droplets in the slag the analysed FeO figure is unreliable and suggest that the progress of the reaction

$$(SiO_2) + 2C = \underline{Si} + 2CO$$

be taken as being indicative of the degree of reduction. The degree to which the reaction had taken place would of course be measured not by $\frac{\%Si}{\%SiO_2}$ but by $\frac{a_{Si}}{a_{SiO_2}}$ and this latter ratio, in view of the lack of knowledge of activities in the complex iron and slag solutions present in the blast furnace, would at present be impossible to evaluate.

An equilibrium study of the reaction

$$\underline{FeS} + C_{gr} + (CaO) = (CaS) + Fe + CO$$

was first made by Hatch and Chipman[2]. In their experiments the FeS was dissolved in carbon saturated iron contained in graphite crucibles and the CaO and CaS were present in a $CaO - MgO - Al_2O_3 - SiO_2$ slag. The authors found that at 1500°C the reaction came to equilibrium very slowly as did also the reaction

$$(SiO_2) + 2C = \underline{Si} + 2CO$$

which was also occurring. No attempt was made to study this second reaction systematically but for the sulphur reaction it was found that

the ratio $\frac{\%S_{slag}}{\%S_{metal}}$ was proportional to the basicity of the slag when measured by an empirical index which they termed "excess base" and which was equal to $(CaO+2/3\ MgO) - (SiO_2+Al_2O_3)$. The authors also found that increase in temperature caused an increase in the sulphur ratio although the effect was small. It could also be said qualitatively that for a given slag basicity an increase in temperature caused an increase in the silicon content of the metal.

This equilibrium study having shown that the above two reactions proceeded very slowly, Grant, Kalling and Chipman[7] and Grant, Troili and Chipman [8] studied the kinetics of the reactions.

Grant, Kalling and Chipman[7] in their study of the effect of MnO additions on the desulphurisation reaction found that the additio n of MnO to the melted slag caused an immediate reversion of sulphur from slag to metal. On further heating, however, the sulphur content of the metal rapidly returned to the value previous to the MnO addition and desulphurisation then proceeded as if no addition had been made. The authors explain that on the addition of MnO there is a large increase in the oxidising power of the slag which causes sulphur to pass from slag to metal according to the reaction

$$(CaS)+\underline{O}=(CaO)+\underline{S}$$

When the reaction

$$(MnO)+C=\underline{Mn}+CO$$

has come to equilibrium the oxygen potential of the MnO is the same as that of CO at that particular temperature. The authors also found that the basicity of the slag had a marked effect on the time required to reach sulphur equilibrium, heats with basic slags coming to equilibrium much more quickly than those with acid slags. From this latter finding the authors deduced that the reduction of silica affected the rate of sulphur transfer. To add further strength to their argument they quote the results of a heat in which a lime alumina slag free from silica was used. In this experiment the sulphur came to equilibrium within 40 minutes of the first slag addition as compared with 5 or 6 hours for silica containing slags.

Grant, Troili and Chipman[8] made further investigations of the effect of silica reduction on the rate of desulphurisation. They found that although silicon in the metal had little effect on the final equilibrium position it strongly affected the rate at which equilibrium was approached. For example, with one particular slag sulphur equilibrium was only attained after 7 hours at 1525°C when there was no silicon present in the metal initially whereas with 2, 3 or 4% silicon added the system came to equilibrium with regard to sulphur after 2 to 3 hours. The authors concluded from their experiments that silica influenced the desulphurisation reaction in a manner similar to MnO. i.e. in the reaction for the reversion of sulphur from slag to metal

$$(CaS) + \underline{O} = (CaO) + \underline{S}$$

the oxygen involved may be from silica as well as from MnO and FeO. When silicon is added to the metal in amounts equal to or greater than the quantity in equilibrium with the particular slag then there is no tendency for the reduction of silica and the slag therefore loses its oxidising power. The authors concluded that it is the slow reduction of silica which prevents the sulphur equilibrium from coming more quickly to equilibrium.

In view of this effect of silica reduction on the rate of desulphurisation, Fulton, Grant and Chipman[3] made a more detailed study of the reaction

$$(SiO_2) + 2C_{gr.} = \underline{Si} + 2CO.$$

The object of the investigation was to provide values of the silicon content of metal in equilibrium with slags of varying composition. Thus in future studies of the kinetics of the sulphur reaction, slag-metal combinations in equilibrium with respect to silicon could be employed and the factor of silica reduction thereby eliminated. The authors confirmed what had previously been found regarding the slowness of the reduction of silica but, by using an experimental method in which progressively larger initial silicon contents were added to the metal until the reaction proceeded in the opposite direction to that written above, they were able to fix the equilibrium silicon content with an estimated accuracy of $\pm$ 1%. They investigated slags of varying lime-silica ratios at the three alumina levels 0,

10 and 20%. Their experiments were confined to the one temperature, 1600°C and their results are shown in graphical form in Fig. (2). As would be expected for any one alumina content the equilibrium silicon in the metal increases with decreasing lime-silica ratio. At high lime silica ratios (above about 1.3) the equilibrium silicon content increases with increasing alumina content whereas at low lime silica ratios the reverse is true, i.e. the results illustrate the amphoteric nature of Al_2O_3 which behaves as a base in acid slags and as an acid in basic slags. In general the silicon contents are much higher than those obtained in blast furnace practice. This is probably due in part to the fact that the temperature of 1600°C used in the experiments is higher than that normally found in the hearth of the blast furnace and partly due to the non-attainment of equilibrium of the reaction

$$(SiO_2) + 2C_{gr.} = \underline{Si} + 2CO$$

in the blast furnace.

Also shown in Fig. (2) are some of the results obtained by Sawamura and Sawamura[9] in a study similar to that conducted by Fulton, Grant and Chipman. The results are much lower than those obtained by the latter authors and it is unlikely in view of the known slowness of the reaction that equilibrium was reached in the short time (ca 4 hours) of their experiments.

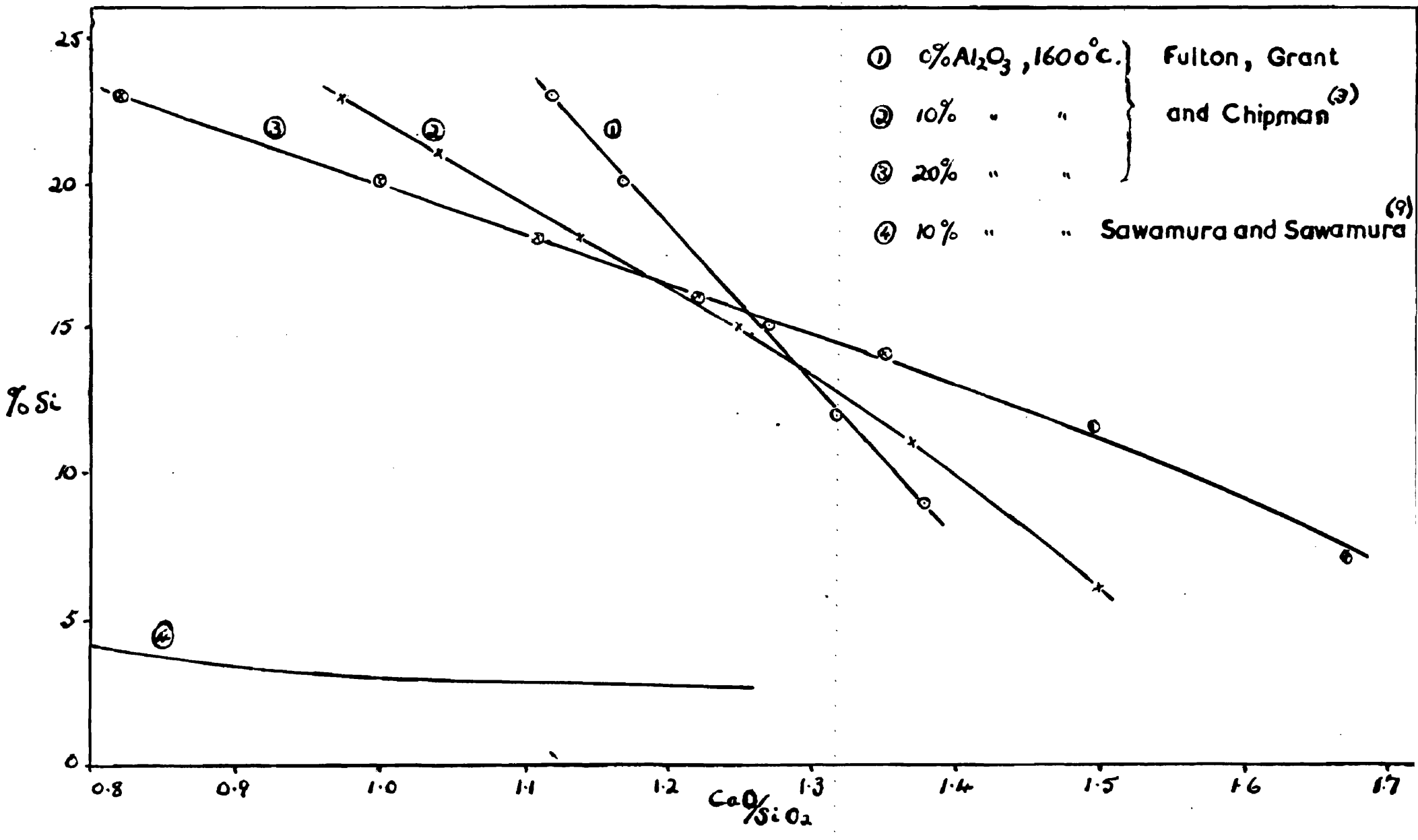


Fig. (2) Variation of the equilibrium silicon content with lime-silica ratio

Although very little direct work has been done on the reaction

$$(2FeO) + \underline{Si} = (SiO_2) + \underline{2Fe}$$

several investigaters have studied the reaction indirectly by means of gas-metal reactions.

Zapffe and Sims[10] studied the reaction

$$(SiC_2) + 2H_2 = \underline{Si} + 2H_2O$$

which reaction can be split up into

$$2H_2O = 2\underline{O} + 2H_2$$

and $$\underline{Si} + 2\underline{O} = SiO_2$$

The authors passed gas mixtures of varying $\frac{H_2O}{H_2}$ ratios over silicon containing metal contained in silica crucibles. Most of the work was done at 1600°C although some runs were also done at 1550°C. Calculating the activity of FeO in the metal from the gas composition and previous results of Fontana and Chipman[11] on the reaction

$$2H_2 + \underline{O} = 2H_2O$$

they found that the product $[\Sigma Si]\ [a_{FeO}]^2$, where $[\Sigma Si]$ is the total silicon content of the metal, was not a constant. The product however varied in a regular manner, high values corresponding to high FeO

activities and low silicon contents. In view of the fact that at high oxygen activities the product $[\Sigma Si]\ [a_{FeO}]$ was a constant the authors made the assumption that the silicon was present mainly as silicon monoxide so that the reaction for the oxidation of silicon would be

$$\underline{SiO} + \underline{O} = SiO_2$$

As this reaction only invloves one atom of oxygen the product $[Si]\ [a_{FeO}]$ would be constant. The authors consider that as Si and SiO are both reduced forms of SiO_2 both must increase as the oxygen potential decreases. Under highly reducing conditions $[\Sigma Si]$ comprises principally $[Si]$ in spite of the fact that $[SiO]$ is also at a maximum. With increasing oxygen potential both $[Si]$ and $[SiO]$ decrease but $[Si]$ decreases much more rapidly that $[SiO]$ so that at high activities of oxygen in the metal $[SiO]$ is the predominating form. Although this hypothesis involving the presence of SiO in liquid iron may not be correct the results of Zapffe and Sims would indicate that the activity of silicon is lowered by the presence of oxygen in the metal.

Gokcen and Chipman[12] in a more careful study of the reactions between hydrogen-water vapour mixtures and silicon containing metal in silica crucibles also found that the equilibrium "constants" for reactions:-

$$H_2 + \underline{O} = H_2O \qquad K_1 = \frac{P_{H_2O}}{P_{H_2} \times \% \underline{O}}$$

$$SiO_2 + 2H_2 = \underline{Si} + 2H_2O \qquad K_2 = \frac{(p_{H_2O})^2}{(p_{H_2})^2} \times \%Si$$

were varying.

From the variation in K_2 with percentage of silicon the authors were able to determine the activity coefficient of silicon. The results also indicated that at low percentages of silicon (<0.3%) the activities of both oxygen and silicon were mutually lowered by the presence of the other element.

Making use of the available thermodynamic data on the reaction

$$2H_2 + O_2 = 2H_2O$$

the oxygen potential corresponding to various $\frac{H_2O}{H_2}$ ratios can be calculated. In Fig. (3) are shown the equilibrium silicon contents of iron in contact with solid silica at 1600°C plotted against the oxygen potential obtained in this way. As can be seen the silicon content increases rapidly as the oxygen potential is decreased below -100 k. cals.

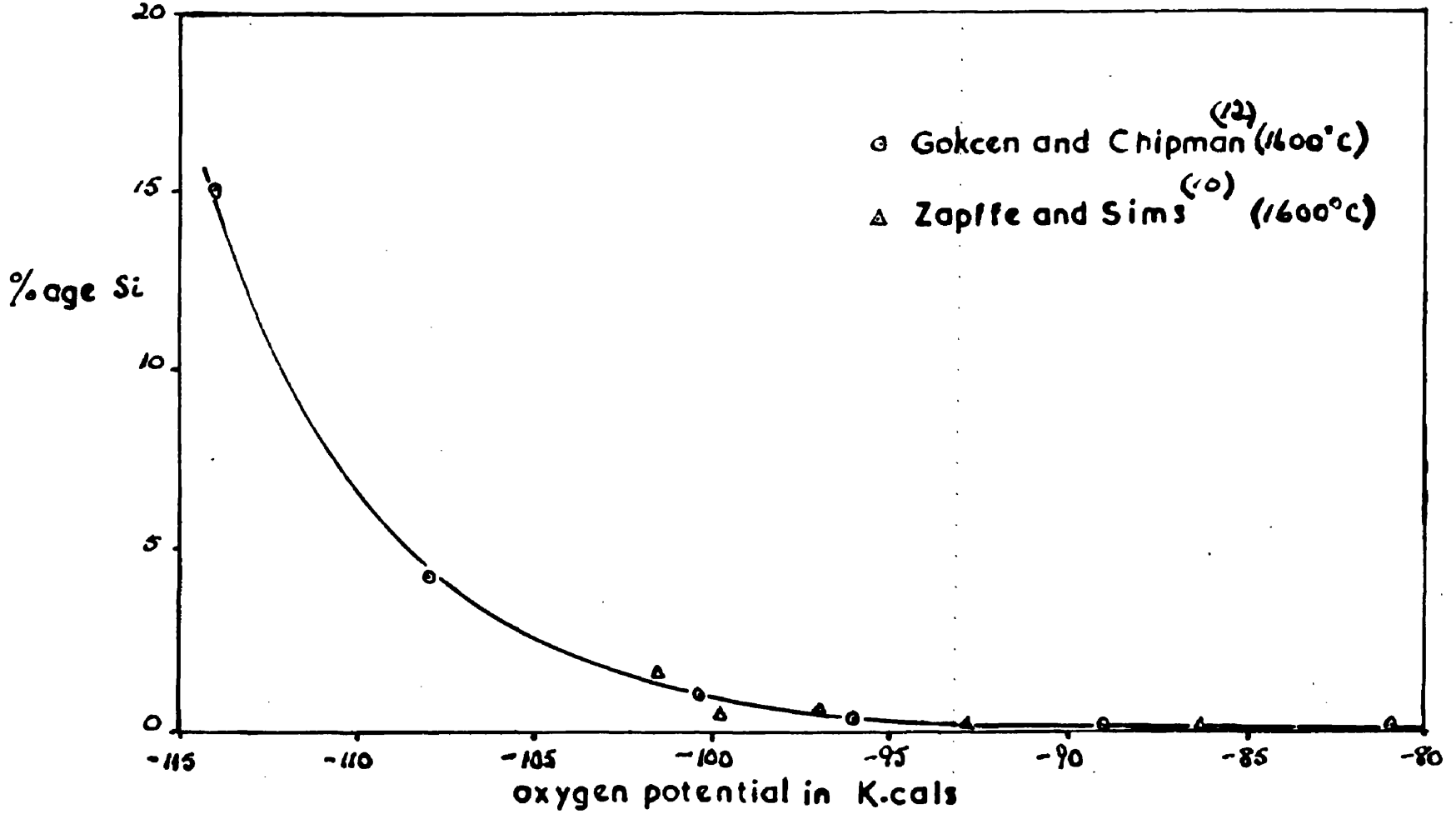


Fig.(3) Effect of varying oxygen potential on the equilibrium silicon content of iron in contact with silica at 1600°C

3. EXPERIMENTAL PROCEDURE.

(a) The Furnace

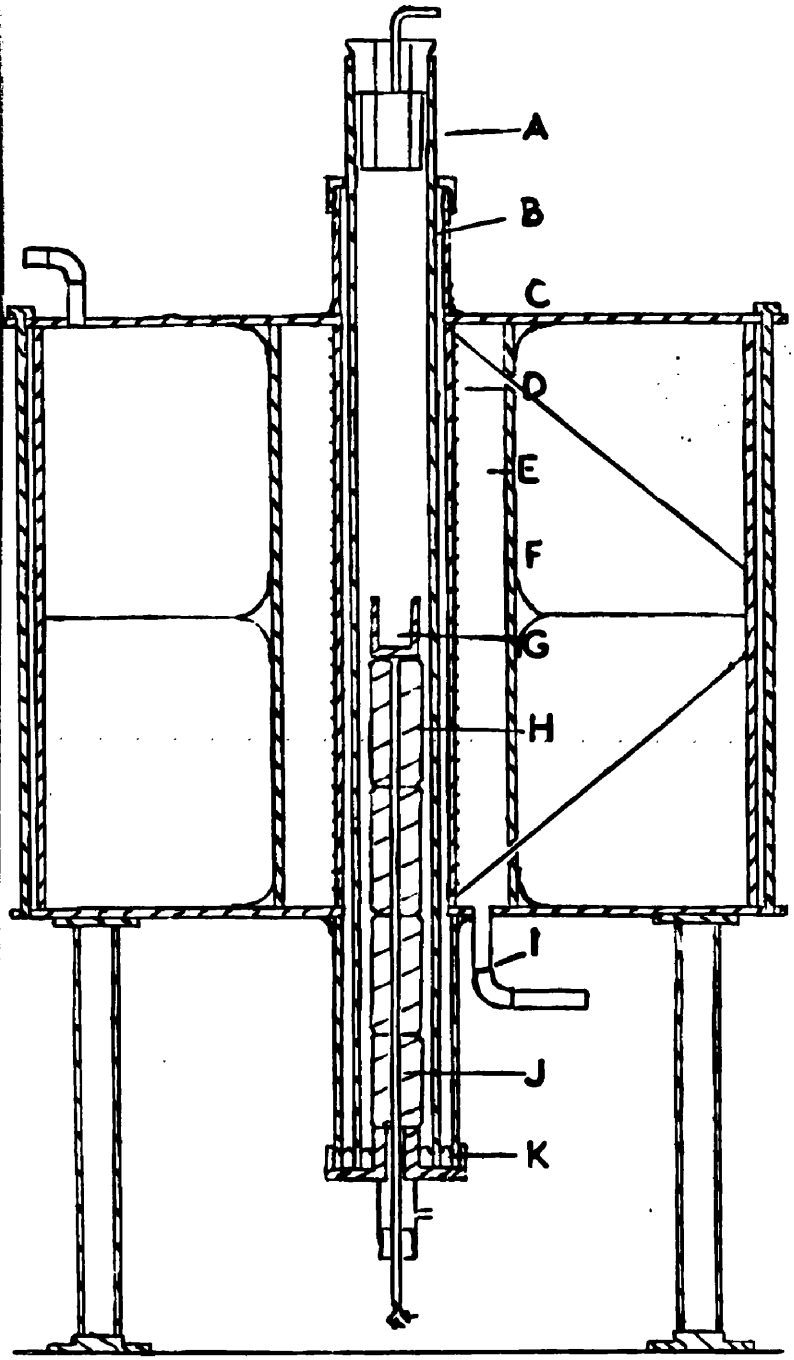
The furnace used in the experiments is shown diagrammatically in Fig. (4). The heating element, 0.040" molybdenum wire, was spirally wound on an alumina tube. Approximately forty feet of wire was used, wound over 14 inches of the alumina tube. In the annulus between the winding and another alumina tube, approximately 6 inches in diameter, were fused alumina granules which served as a high temperature insulating material. Further insulatinn was provided by insulating fire-brick between the secondary alumina tube and the steel furnace walls. The innermost tube, in which the crucible was supported on refractory stools, was of impervious mullite.

Owing to the ease with which molybdenum is oxidised above red heat a reducing atmosphere must be maintained within the furnace. For this purpose cracked ammonia was used. The ammonia gas was passed over red hot iron turnings where the reaction

$$2NH_3 = N_2 + 3H_2$$

took place. The cracked ammonia was first washed free of ammonia and then dried before entering the furnace by means of inlet tube (I).

A liquid metal seal was provided at the base of the furnace in order to prevent the entry of air. This seal is shown in enlarged form in Fig. (4a). The inner mullite tube rested in a pool of Wood's metal which, as well as preventing the inlet of air, effectively separated the atmosphere of the inner tube from that surrounding the



A mullite tube

B space for packing material

C steel casing

D molybdenum wound alundum tube

E fused alumina granules

F alundum tube

G crucible

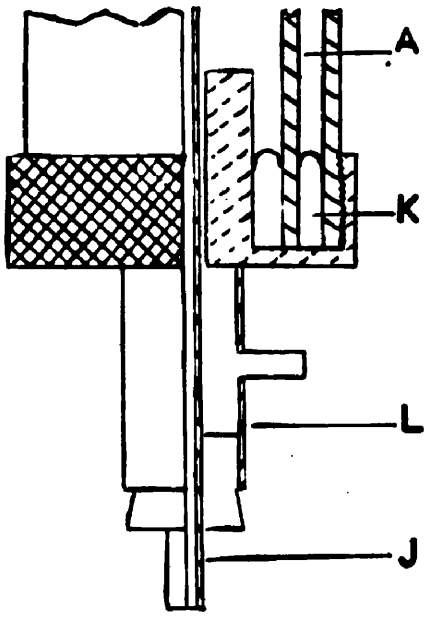
H refractory stools

I inlet for cracked ammonia

J thermocouple sheath

K Woods metal

L brass tube



(4) Schematic view of furnace

Fig. 4(a)

winding. The Wood's metal was contained in an annulus machined in a brass cap which was threaded on to a steel tube welded to the base of the furnace. The thermocouple sheath (J) was introduced through the centre of the brass cap and this opening made gas tight by a brass tube (L) brazed to the cap and fitted with a rubber bung. In the brass tube was provided a small opening through which the desired atmosphere could be introduced to the inner working tube.

At the top of the furnace was fitted a packing gland, filled with asbestos rope, again to prevent the entry of air into the furnace.

Temperature measurement was made by means of a platinum-platinum + 13% rhodium thermocouple contained in the thermocouple sheath (J).

Temperature control in the earlier runs was made by means of a variable resistance and in the later runs by means of a Sunvic energy regulator.

(b) Crucibles

In the study of slag-metal equilibria the problem arises as to what material can be used to form a crucible which will contain both slag and metal. In the case of carbon saturated iron and slags free from ferrous oxide graphite can, of course, be used. When it is desired to investigate slags containing FeO, however, non-reducing material such as refractory oxides must be used. Using such oxides, contamination of the slag by the crucible material becomes inevitable and in the present work, as it was desired to keep the slag system as

simple as possible, the choice of crucible material was limited to one of the oxides lime, alumina or silica or to a mixture of these oxides.

Sillimanite and mullite crucibles were initially tried but proved unsatisfactory as they were extensively attacked by the lime-alumina-silica-ferrous oxide slag. These sillimanite crucibles were very porous and it was later found that a dense slip cast sillimanite crucible offered much greater resistance to slag attack. Unfortunately time did not permit a series of experiments to be made in these crucibles.

Alumina crucibles, slip cast and fired to 1650°C were tried but these also were unable to resist slag attack. The problem was eventually solved by fitting a molybdenum sleeve in the alumina crucible so that the slag was in contact with molybdenum and the metal in contact with alumina as illustrated in Fig. (5). With such crucibles it is only possible to work in a limited range of slag composition as the slag becomes saturated with alumina.

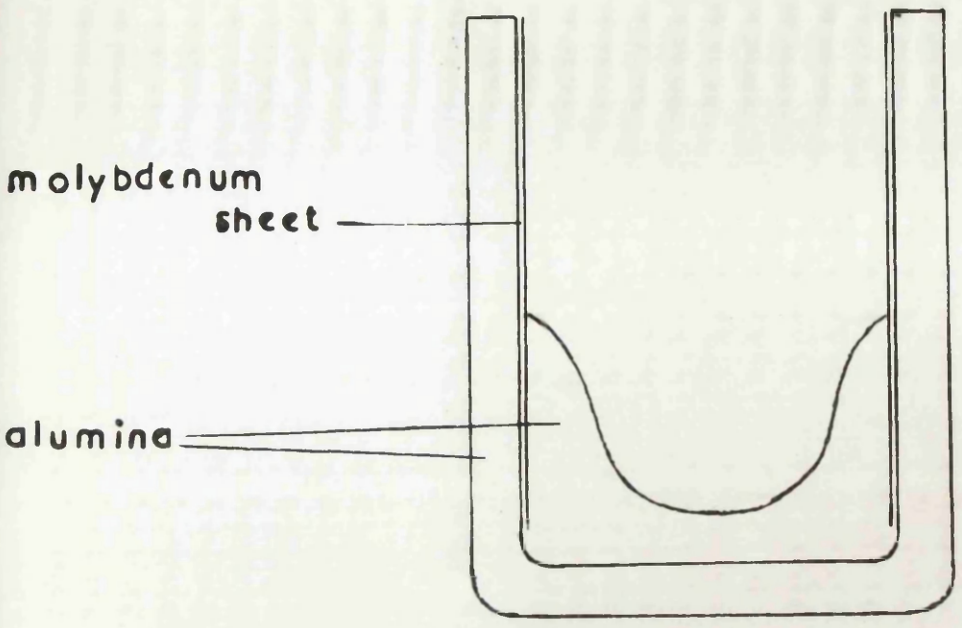
Construction of Crucibles

(i) Graphite crucibles

These crucibles were machined from 2 inch diameter electrode graphite rod and had dimensions:- outside diameter 2 inches, inside diameter 1½ inches and height 4 inches.

(ii) Alumina crucibles

The raw material for the making of alumina crucibles was



Fig(5)Composite alumina molybdenum crucible

Thermal Syndicate C.60 alundum. This was first fired to approximately 1,000°C in order to decompose organic matter which would otherwise have led to porosity in the crucibles. The fired alundum was ground for approximately 16 hours in a steel ball mill and then treated with 25% hydrochloric acid in order to dissolve the iron introduced by ball milling. This acid was then decanted and replaced by weaker acid. This process was repeated until nearly all the iron had been removed. Water was then added until the slip had a creamy consistency and crucibles cast in plaster of paris moulds. It was found with low acid concentrations, i.e. $< 5\%$, that the shrinkage of the crucibles during casting was insufficient to allow their removal from the moulds. Even with 5% acid in the slip the interior of the moulds was dusted with french chalk prior to casting in order to facilitate the removal of the crucibles.

After removal from the moulds the crucibles were air dried at room temperature for several days or for a shorter time at a higher temperature. The crucibles were then fired to about 1000°C and their interior smoothed with emery paper. Higher firing was then employed in order to develop strength in the crucibles and the 0.5 m.m. thick molybdenum fitted. An alundum cup was then moulded inside the molybdenum and the whole dried and fired to 1600°C in a reducing atmosphere. In use, the metal filled the cup and was thus in contact with alumina whereas the

slag resting on top of the metal was in contact with molybdenum and the ring of alundum round the metal. A certain amount of penetration of the slag occurred in this annulus and although in most cases it was not extensive it did sometimes lead to failure of the crucible. Slag also managed to penetrate to the alumina crucible at the overlap of the molybdenum sheet if this was insufficient. i.e. $< \frac{3}{8}$ inches. Failure from these and other, unknown, causes amounted to about 50% of the total number of crucibles used.

(c) Preparation of Metal and Slag

(i) Metal

The metal used in all the runs was iron containing varying quantities of silicon and saturated with carbon at 1500°C. It had been found in preliminary experiments that a considerable time was required for the solution of ferrosilicon in carbon saturated iron contained in a graphite crucible and for this reason the following procedure was adopted. Armco iron and the requisite amount of ferrosilicon was first melted in a fire-clay crucible by means of high frequency induction heating. This alloy was then transferred to a graphite crucible and heated to 1500°C. The temperature was maintained constant for approximately 30 minutes to ensure carbon saturation and the iron then poured into water. The resulting metal was then melted by means of high frequency heating in a small fire-clay crucible of similar

shape to the alundum cup of the alumina-molybdenum crucible. Any scale on the surface of the metal was removed and the metal sampled for analysis.

In experiments done in graphite crucibles, the initial procedure was the same but in this case the iron silicon alloy was transferred into the graphite crucible in which the experiment was to be made.

(ii) Slag

The lime-alumina-silica slag was prepared from silica, alumina and calcium carbonate. Analar alumina and calcium carbonate were used and the silica (99.8% pure) was obtained from ground quartzite from which the iron had been removed by washing with hydrochloric acid.

The raw materials were first fired to about 1100°C in order to decompose the carbonate and allow some sintering to take place. The material was then transferred to a graphite crucible, melted by means of high frequency induction heating and poured into an iron mould. During melting it was important to keep the temperature of the crucible below about 1650°C as above this temperature white fumes of silicon monoxide produced by the reaction

$$SiO_2 + C = SiO + CO$$

were given off resulting in a loss of silica.

The initial sintering at 1100°C permitted a lower temperature to be used in melting than would otherwise have been the case so that the possibility of silica reduction was minimised.

Preparation of FeO

In vacuum, ferrous oxalate decomposes at approximately 650°C according to the equation

$$Fe(COO)_2 = FeO + CO_2 + CO$$

A closed bottom iron tube with several holes drilled along one side to facilitate the expulsion of gas was packed with ferrous oxalate and placed inside a larger iron tube. This tube was then heated at 150°C for about 1 hour to drive off adsorbed moisture, then evacuated, heated to 1000°C, sealed and water quenched. Magnetic material was separated from the product and the remainder mixed and analysed. The material analysed 76.8% Fe showing that there was an excess of oxygen present compared with pure FeO (77.8% Fe).

(d) Experimental Procedure

(i) Experiments in the composite alumina-molybdenum crucibles.

The metal bead containing carbon and silicon and weighing approximately 40 grms. was placed in a composite crucible and about 30 grms. of the premelted slag added. Preliminary runs had shown that a slag with a lime silica ratio of 1.1 contained 41% Al_2O_3 when saturated with alumina. A slag having the composition CaO = 34%; Al_2O_3 = 35% and SiO_2 = 31% was therefore added in order to reduce the amount of attack on the

alundum cup inside the crucible. The composite crucible contained in a small graphite crucible was then placed in the furnace, the purpose of the latter crucible being to protect the furnace tube from slag attack in the event of the composite crucible failing.

During the period when the furnace was heating a reducing atmosphere was maintained within the furnace to prevent oxidation of the molybdenum. When the temperature reached 1500°C the hydrogen was removed from the furnace tube, air introduced, and the tube closed to the atmosphere. Because of the presence of the outer carbon crucible the oxygen in the air burned to carbon monoxide so that during the run the atmosphere was a CO - N_2 mixture containing 35% carbon monoxide. A preliminary experiment had shown that this atmosphere was non-reducing with regard to lime-alumina-silica slags containing small quantities of FeO. This experiment consisted of melting Armco iron and a known weight of slag in a composite crucible and adding a known amount of FeO. After maintaining the temperature at 1500°C for 3 hours the slag was sampled and analysed for FeO. The results are shown in Table (1).

TABLE (1)

FeO added. grm.	Wt. of slag gms.	% FeO calculated	% FeO analysed
1.30	32	3.90	3.95

When the furnace temperature had been steadied at 1500°C a small pellet of FeO and lime was added. The amount of lime incorporated in the pellet being such that if all the FeO reacted with silicon to give silica there would be no change in the lime silica ratio. Another preliminary experiment had shown that approximately $3\frac{1}{2}$ hours were required for the FeO to reach a steady value. The FeO values taken at different times during the run are shown in Table (2) and graphically in Fig. (6).

TABLE (2)

Time after last FeO addition hours	FeO in slag
1	1.50%
2	1.11%
$3\frac{1}{4}$	0.95%
4	0.98%

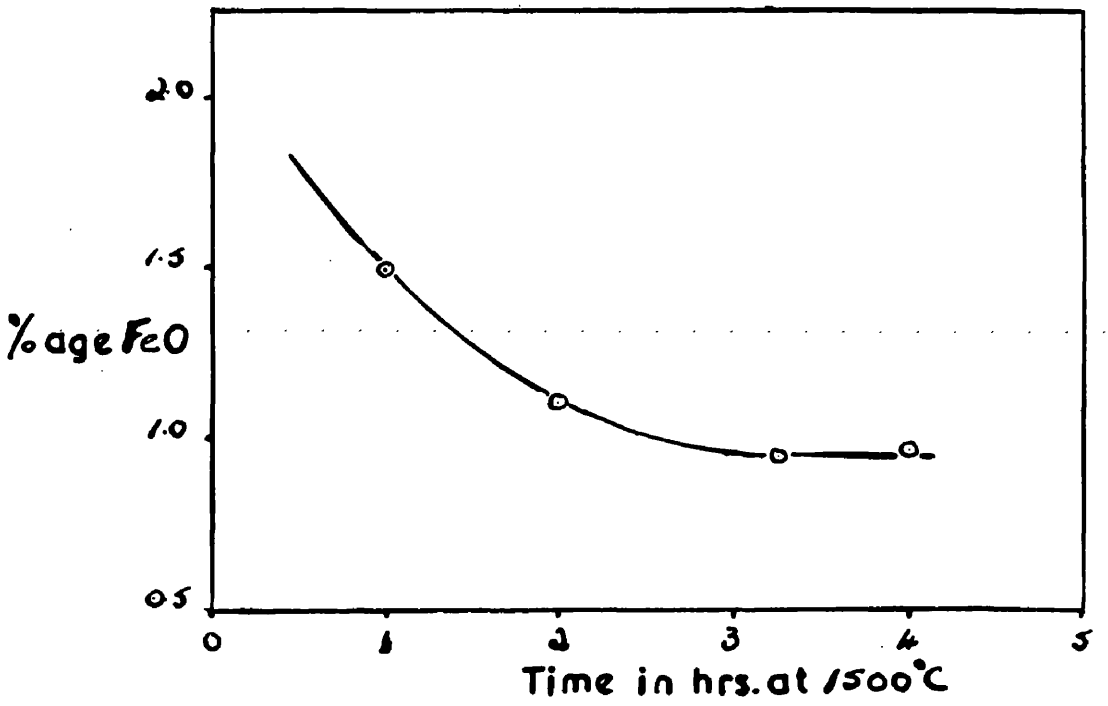


Fig. (6) Approach to equilibrium of FeO content of slag

The furnace temperature was maintained at 1500°C ± 15° during the time of the run which was standardised at 4 - 4½ hours. The slag was then sampled by dipping a brass rod therein and the furnace switched off. In view of the sluggishness of the reactions being studied and the fact that the furnace cooled from 1500°C to 1300°C in 15 minutes the amount of reaction before the slag became solid should have been very small. After cooling, the metal was sampled for analysis.

(ii) The experiments in graphite crucibles

In these experiments the metal was placed in a graphite crucible and heated to 1500°C. After steadying the temperature a metal sample was taken by means of a silica tube to the end of which was attached an aspirator bulb. This is the sample subsequently called the "initial metal" sample. After sampling, the preformed lime-alumina-silica slag was added and the temperature maintained at 1500°C ± 15° during the experiment which was of approximately 7 hours duration. Final metal and slag samples were then taken in the manner described above.

(e) The Partial Pressure of Carbon Monoxide

In both the reactions

(i) $\underline{C} + (FeO) = CO + Fe$

(ii) $(SiO_2) + 2\underline{C} = \underline{Si} + 2CO$

carbon monoxide is one of the resultants so that its partial pressure

affects the equilibrium position of the reactions. As both reactions are taking place at the slag metal interface the effective partial pressure is not that in the atmosphere above the slag but that at the interface. This partial pressure of carbon monoxide is thus the pressure of the bubbles of CO produced by these reactions which in this case was one atmosphere plus the hydrostatic pressure of the slag layer. This latter quantity in these experiments was very small and was therefore neglected.

(f) Analysis of Metal and Slag

Carbon and silicon were determined in the metal samples using the standard methods of chemical analysis.

Difficulty, however, was experienced in the analysis of the slag samples. Silica determinations involving dehydration from hydrochloric acid solution were invariably low whereas the estimation of alumina by precipitation of the hydroxide with subsequent weighing of the oxide gave very inconsistent results. To obviate these difficulties the following method was adopted.

The finely ground slag sample was boiled with water and dissolved by the addition of hydrochloric acid. To the slightly cooled solution concentrated sulphuric acid was added and the solution then evaporated to fumes of SO_3. After cooling, dilute hydrochloric acid was added, the solution boiled and the silica filtered off. The residue remaining after treatment of the silica with hydrofluoric acid in a platinum basin was fused with sodium carbonate, the fusion extracted and added

to the main filtrate. The filtrate was made up to 500 mls. and 100 mls. portion taken for the estimation of lime and alumina. The lime was determined by precipitation of the oxalate. The precipitate was filtered off, washed and dissolved in dilute sulphuric acid. Titration of the liberated oxalic acid in hot solution with standard potassium permanganate solution completed the determination.

Alumina was determined by precipitating aluminium phosphate from a solution buffered by the addition of ammonium acetate. The precipitation was carried out in the presence of sodium thiosulphate which, by destroying the excess acid present, gave a more granular precipitate. The precipitate was filtered off, washed, ignited and weighed as $AlPO_4$.

Estimation of FeO.

In the analysis of slags containing quantities of FeO greater than approximately 0.4% no especial difficulty was encountered. The slag was first finely ground and the major portion of the free iron removed by a small hand magnet. The remainder of the iron was removed by passing the slag under a powerful electromagnet and the estimation of iron carried out by the standard method involving reduction of the ferric iron by stannous chloride followed by titration of the solution with $\frac{N}{50}$ potassium dichromate. This method proved very accurate for slags containing more than 0.4% FeO but with FeO contents below this figure the accuracy deteriorated so that a colorimetric method was

adopted.

After subjecting the slag to the magnetic treatment as before, a sample was dissolved in hydrochloric acid, the silica removed as described above and the residue remaining after treatment of the silica with hydrofluoric acid again added to the main filtrate. The iron in this solution was estimated by taking an aliquot portion, forming the red coloured complex between ferrous iron and ortho-phenanthroline and determining the intensity of the colour by means of the Spekker absorptiometer. To ensure that all the iron was present in the ferrous state, the reducing agent hydroxylamine hydrochloride was first added together with sodium acetate, the function of the latter being to maintain the solution at a pH of 4.5 at which acidity the coloured complex is most stable.

4. DISCUSSION OF ACTIVITIES IN LIQUID METALS AND SLAGS.

(a) Introduction

In the study of slag-metal equilibria thermodynamic data can be used to determine the ratio of the activity of an element in the metal phase to the activity of its oxide in the slag phase. Before such information can be put to practical use, however, the relationship between activity and concentration must be known.

The activity of a substance M in solution is defined by the equation

$$G_M - G^o_M = RT \log_e a_M$$

where G_M and G^o_M are the free energies per mole of the substance M in solution and in some chosen standard state respectively and a_M is the activity of M in the solution. The activity is thus a relative function; its actual value depending on the choice of standard state. Although thermodynamically any state could be chosen as the standard it has been found that certain ones are more convenient than others.

In the case of solid or liquid solvents the pure substance at each temperature is taken as the standard state of unit activity. The ratio $\frac{a}{N}$, where N is the mole fraction of the solvent, is known as the activity coefficent and is usually denoted by the symbol γ. In certain cases, e.g. in dilute solutions, the employment of the pure substance as the standard state for the solute proves to be unnecessarily cumbersome and a more convenient standard state is adopted. If C_M is the concentration of the solute in weight percent, then this standard state is so defined that $\frac{a_M}{C_M}$ approaches unity as C_M tends to

zero.

This scale of activities, in which the activity coefficient $\frac{a}{C}$ is designated by f, has proved to be the most convenient in the case of liquid metallic solutions.

Change of Scale.

Frequently when dealing with activities it is convenient if an activity value measured on one of the above scales can be converted to the corresponding value on the other scale. This change of scale can be effected provided the free energy change accompanying the transfer of one gram molecule of the substance from the pure state to the dilute solution of unit activity is known.

For example in the case of silicon in iron at 1600°C

$$Si_{(liq)} = Si_{(dil.sol'n.)} \qquad \Delta G^{\circ} = -27,200 \text{ cals.}$$

Now $$\Delta G^{\circ} = G_{\text{dil sol'n.}} - G_{(liq)} = RT \log_e \frac{a_{Si\ (dil.sol'n)}}{a_{Si\ (liq)}}$$

so that $$\frac{a_{Si\ (d.s.)}}{a_{Si\ (liq)}} = 0.0007.$$

Where $Si_{(liq)}$ denotes pure liquid silicon and $Si_{(dil.\ sol'n.)}$ denotes the dilute solution of silicon in iron in which the activity of silicon is unity on the scale in which activity is equal to percentage at infinite dilution. Thus on the dilute solution scale $a_{Si\ (d.s.)}=1$

and the activity of pure liquid silicon on this scale is $\frac{1}{0.0007} = 1.43 \times 10^3$. On the pure scale ${}^{a}Si_{(liq)} = 1$ and ${}^{a}Si$ (dil.sol'n) = 0.0007. To convert values of the activity of silicon on the dilute solution scale to values on the pure scale at 1600°C it is thus necessary to multiply by 0.0007.

Variation of the activity coefficient with temperature

The variation with temperature of the activity co-efficient of a substance M in solution is given by the formula

$$d \log_e f_M = \frac{\bar{L}_M}{RT^2}$$

where $\bar{L}_M = \bar{H}_M - \bar{H}^o_M$ is the partial molal heat content of M referred to the standard state. In the case of dilute solutions it is unlikely that the value of $\bar{L}$ will be large because such solutions do not differ greatly in composition from the standard state. The few values of $\bar{L}$ which have been determined over the relevant range of compositions confirm this view[13].

Activities of substances of interest in the present work

In this work the reactions which have been studied are

(1) $\underline{Si} + 2(FeO) = (SiO_2) + 2\underline{Fe}$.

(2) $\underline{C} + (FeO) = CO + \underline{Fe}$

and (3) $(SiO_2) + 2C_{gr.} = \underline{Si} + 2CO$

where the substances underlined were present in the metal phase consisting of iron, carbon and silicon and those bracketed in the slag phase consisting of CaO, Al_2O_3, SiO_2 and FeO. The three reactions were studied at 1500°C and the standard free energy change accompanying each reaction can be calculated from the known free energy of formation of the various substances participating. Thus for reaction (1)

$$Si + O_2 = SiO_2 \qquad \Delta G^\circ = -217,600 + 48.79T$$

$$2Fe + O_2 = 2FeO \qquad \Delta G^\circ = -111,250 + 21.67T$$

$$Si + 2FeO = SiO_2 + 2Fe \qquad \Delta G^\circ = -106,250 + 27.12T$$

so that at 1500°C $\Delta G^\circ = -58,350.$

A similar procedure for reactions (2) and (3) yields values of ΔG° of -27,570 cals. and +3,400 cals. respectively.

Thus

$$\Delta G_1^\circ = -58,350 \text{ cals.} = -RT \log_e K_1' \text{ where } K_1' = \frac{a_{SiO_2} \times a^2_{Fe}}{a_{Si} \times a^2_{FeO}}$$

$$\Delta G_2^\circ = -27,570 \text{ cals.} = -RT \log_e K_2' \text{ where } K_2' = \frac{a_{Fe} \times p_{CO}}{a_C \times a_{FeO}}$$

$$\Delta G_3^\circ = +3,400 \text{ cals.} = -RT \log_e K_3' \text{ where } K_3' = \frac{a_{Si} \times p^2_{CO}}{a_{SiO_2} \times a^2_C}$$

In order to convert these equilibrium constants into terms of percentages the relationship between activity and weight concentration of

(a) SiO_2 and FeO in the CaO Al_2O_3 - SiO_2 - FeO slag and

(b) C, Si and Fe in the metal phase are required.

Some of these activities have been investigated experimentally but in most cases there still exists some dubiety as to the true value. In order to assess the accuracy of the various values a critical survey of the existing data will be given.

(b) (i) <u>The activity of silicon in molten iron</u>

The activity of silicon in molten iron silicon alloys at 1600°C has been derived by Chipman[13] from the iron-silicon phase diagram of Houghton and Becker[14]. At the high silicon end of the diagram where pure silicon is the primary solid phase then the activity of silicon in the liquid at the liquidus temperature is the same as that of the solid silicon separating. From the known heat of fusion of silicon and the change of specific heat involved in fusion[15] these activities can then be calculated relative to the super cooled liquid at the particular liquidus temperature. In the region of the diagram where the compound FeSi is the primary phase, Chipman has utilised a formula derived by Hauffe and Wagner[16] in calculating the activity of silicon at the liquidus temperature. Thus values of the activity of silicon at the liquidus temperature can be calculated

from the phase diagram in the range 100 to 20% silicon. In order to calculate the activities at temperatures other than the liquidus Chipman has used a semi-empirical formula

$RT\log_e \gamma_1 = bN_2^2$ where γ_1 denotes

the activity coefficient of one of the components in a binary solution, N_2 the mol fraction of the other and b is a constant. It is not possible to calculate the activity of silicon in the range 0~20% silicon from the phase diagram and use has been made of the data available at the time on the deoxidation of steel by silicon in order to determine relative to the pure liquid, the activity of silicon in very dilute solutions.

Thus:

(1) $SiO_2 = Si_{(in Fe)} + 2O_{(in\ Fe)}$ $\quad \Delta G^\circ_{1600^\circ C} = 38{,}100$ cals.

(2) $O_{2(gas)} = 2O_{(in\ Fe)}$ $\quad \Delta G^\circ_{1600^\circ C} = -58{,}500$ cals.

Subtraction gives

(3) $SiO_2 = Si_{(in\ Fe)} + O_{2(gas)}$ $\quad \Delta G^\circ_{1600^\circ C} = +96{,}600$ cals.

and

(4) $O_{2(gas)} + Si_{(liq)} = SiO_2$ $\quad \Delta G^\circ_{1600^\circ C} = -126{,}300$ cals.

---

so that

(5) $Si_{(liq)} = Si_{(in\ Fe)}$ $\quad \Delta G^\circ_{1600^\circ C} = -29{,}700$ cals.

By using the equation

$$\Delta G^{\circ} = RT\log_e \left(\frac{a_{Si\ (dil\ sol'n.)}}{a_{Si\ (liq.)}} \right)$$

the activity of silicon on the pure scale of the standard dilute solution was then calculated. To obtain values of the activity coefficient from 20% to 1% silicon Chipman[13] interpolated between the values obtained at these compositions. In view of this rather lengthy interpolation and also the fact that in subsequent work[12] a different values of ΔG° for reaction (1) has been obtained, too much reliance cannot be placed on the values of the activity coefficient in the range 0 - 20% silicon.

Gokcen and Chipman[12] in their study of the reaction between hydrogen-water vapour mixtures and silicon dissolved in iron at 1600°C, have also obtained values for the activity coefficient of silicon. For this reaction

$$SiO_2 + 2H_2 = Si + 2H_2O$$

$$K = \frac{a_{Si} \times p^2_{H_2O}}{a_{SiO_2} \times p^2_{H_2}}$$

As the metal was contained in silica crucibles the activity of silica is unity so that the constant reduces to,

$$K = \frac{a_{Si} \times p^2_{H_2O}}{p^2_{H_2}}$$

The non-constancy of the product $\%Si \times \frac{p^2_{H_2O}}{p^2_{H_2}}$ could thus be attributed to a variation in the activity coeffieient of silicon f_{Si} where $f_{Si} \times \% Si = a_{Si}$. These values differ appreciably from those previously derived by Chipman, Fig. (7). However, in view of the criticisms which have been made above of these latter values, the results of Gokcen and Chipman[12] have been taken as being the more reliable.

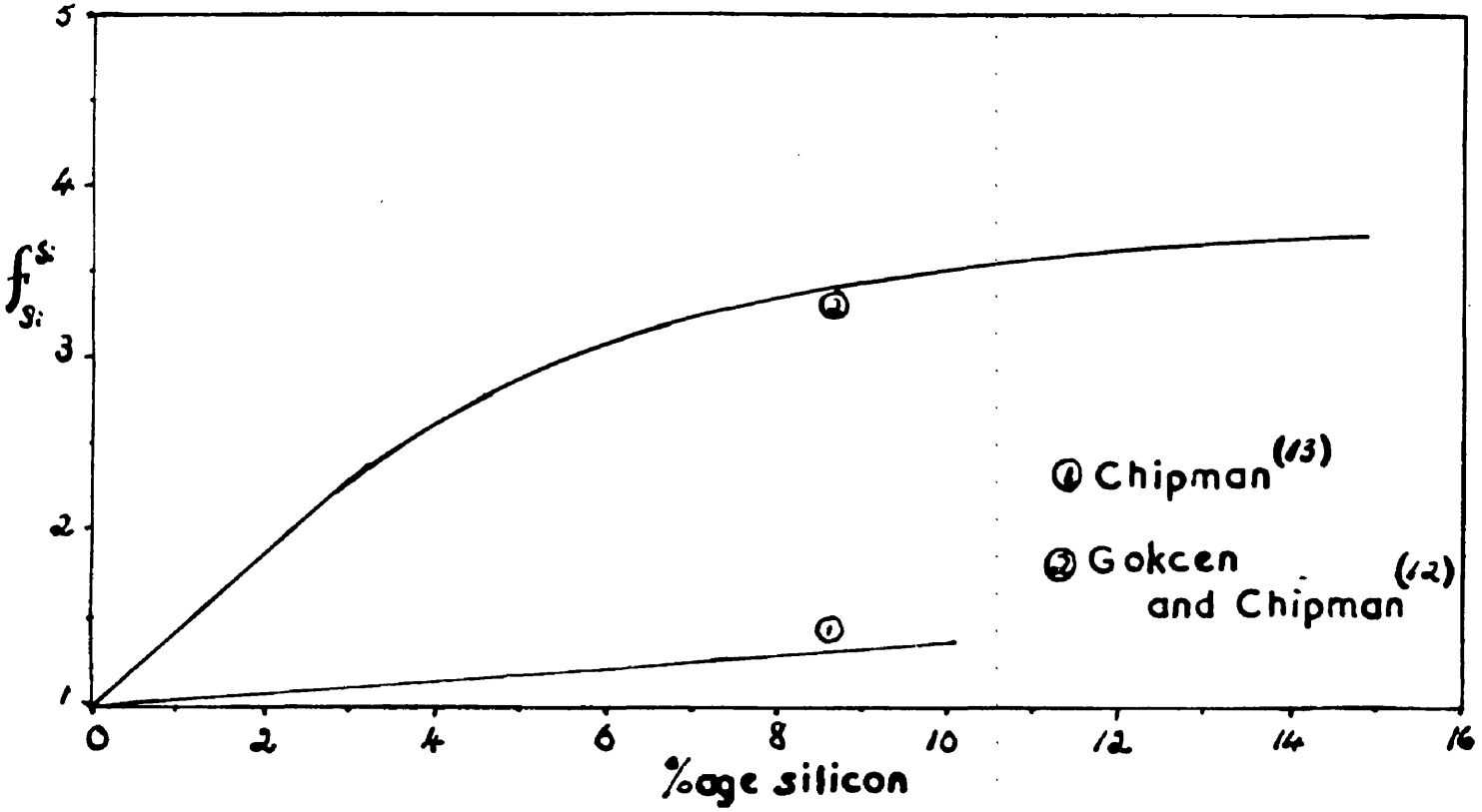
Both sets of values shown in Fig. (7) are strictly speaking only applicable at 1600°C. In the present work, however, it has been assumed that the error introduced in applying them at 1500°C is small. The justification for this assumption is explained earlier in this chapter. (p.34).

It is also possible from the work of Gokcen and Chipman[12] to calculate a value of the free energy of solution of silicon in iron. The value, at 1600°C, of K for the reaction,

$$SiO_2 + 2H_2 = \underline{Si} + 2H_2O$$

was found to be 2.5×10^{-4} so that the free energy change ($-RT\log_e K$) is +30,900 cals. By combining this value with the known free energy changes accompanying the formation of silica and water vapour the free energy change accompanying the reaction

$$Si_{(liq)} = Si_{(dil\ sol'n\ in\ Fe)}$$ can be calculated.



Fig(7) Variation of the activity coefficient of silicon with silicon content

Thus;

$SiO_2 + 2H_2 = \underline{Si} + 2H_2O$	$\Delta G^\circ_{1600^\circ C} = +30,900$ cals.
$Si_{(liq)} + O_2 = SiO_2$	$\Delta G^\circ_{1600^\circ C} = -126,100$
$Si_{(liq)} + O_2 + 2H_2 = \underline{Si} + 2H_2O$	$\Delta G^\circ_{1600^\circ C} = -95,200$
$2H_2 + O_2 = 2H_2O$	$\Delta G^\circ_{1600^\circ C} = -68,000$
$Si_{(liq)} = \underline{Si}$	$\Delta G^\circ_{1600^\circ C} = -27,200$

This value differs appreciably from that calculated by Chipman[13] but, as it has been obtained without using the uncertain data on the reaction

$$SiO_2 = \underline{Si} + 2\underline{O}$$

from which the latter value was calculated, has been considered as being the more reliable.

At 1600°C as has been shown (p.33), this value yields a ratio of activities on the two scales of measurement of 0.0007. By analogy with other elements the entropy change accompanying the reaction,

$$Si_{(liq)} = \underline{Si}$$

should be small[17] so that the error introduced in assuming that the value of the free energy change for the reaction does not vary between

1600°C and 1500°C will be small. Making this assumption the ratio of activities on the two scales of measurement is found to be 0.00047 at 1500°C.

(ii) The effect of Carbon on the Activity Coefficient of Silicon

The values of the activity coefficient of silicon obtained by Chipman[13] and by Chipman and Gokcen[12] apply only to iron silicon alloys and when one is dealing with iron-carbon-silicon alloys the effect of carbon on this activity coefficient must be known before the activity of silicon can be calculated. Chipman[13] has calculated this effect from results obtained by Körber[18] in his study of the effect of carbon additions on the equilibrium position of the reaction

$$SiO_2 + 2Mn = 2(MnO) + \underline{Si}$$

The equilibrium constant for this reaction is given by the equation

$$K = \frac{a^2_{MnO} \times a_{Si}}{a_{SiO_2} \times a^2_{Mn}}$$

As the slag was saturated with solid silica, a_{SiO_2} is unity and as there were only small variations in the MnO content of the slag it was assumed that a_{MnO} was constant. The solution of manganese in iron has been found to be ideal[19] so that the activity of manganese can be taken as equal to its weight percentage. The equation thus becomes

$$K' = \frac{f_{Si} \times \% Si}{(\% Mn)^2}$$

i.e. for any given manganese content, the activity of silicon is fixed.

The decrease in the ratio $\frac{\%Si}{(\%Mn)^2}$ which Körber found on the addition of carbon to the metal must therefore be attributed to an increase in the activity coefficient of silicon.

When discussing the activity coefficient of silicon in ternary solutions it is convenient to divide the coefficient into its constituents. Thus if f_{Si} is the activity coefficient in the ternary solution and f_{Si}^{Si} is the corresponding coefficient in plain iron-silicon alloys then the effect which carbon has on the activity coefficient of silicon, f_{Si}^{C}, is given by the equation

$$f_{Si}^{C} = \frac{f_{Si}}{f_{Si}^{Si}} \quad \text{i.e.} \quad f_{Si} = f_{Si}^{Si} \times f_{Si}^{C}$$

So far the nomenclature regarding activity coefficients in ternary solutions has not been standardised and numerous systems exist in the literature. In the present work, however, the system indicated above will be used, i.e. in general, f_{x}^{A} denotes the effect of A on the activity coefficient of x, f_{x}^{x} is the activity coefficient of x in the plain iron-x solution and f_x is the overall activity coefficient of x in the ternary solution.

Values of f_{Si}^{C} have been calculated by Chipman[13] in the range 0-4%C and these are shown in Fig. (8). The main critisism which can be brought against these values is that in many of Körber's original experiments[18] it was assumed that metal and slag had come to equilibrium in times as short as 30 minutes. Similar reactions,

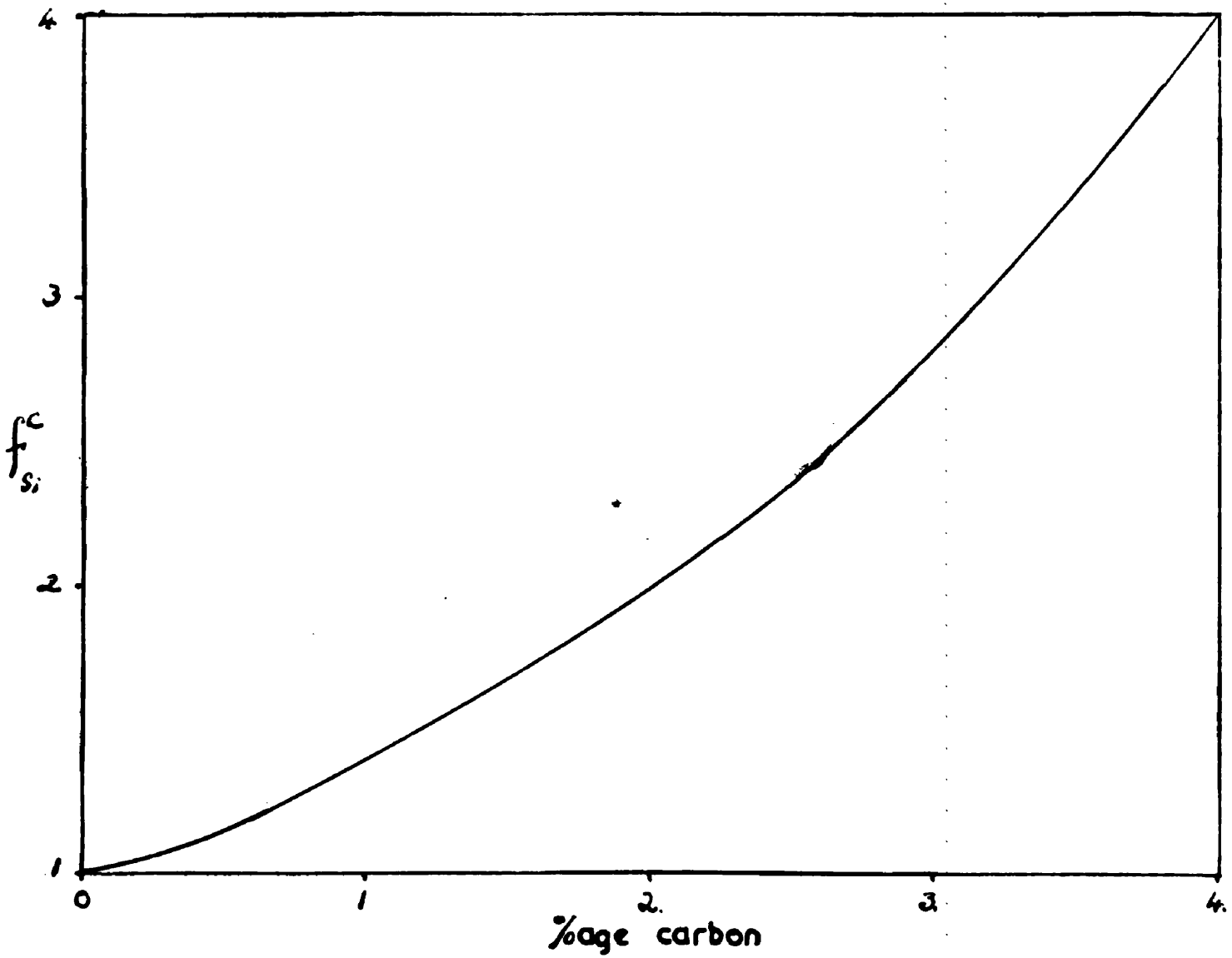


Fig.(8) Effect of carbon on the activity coefficient of silicon

involving slags more fluid than the highly siliceous ones of Körber, have been found[20] to require longer times to come to equilibrium and for this reason the values calculated by Chipman[13] cannot be considered as being more than approximately correct.

(c) (i) The Activity of Carbon in Liquid Iron

Using the results of Marshall and Chipman[21] in their study of the reaction

$$\underline{C} + CO_2 = 2CO$$

at 1540°C, Chipman[13] has calculated the activity of carbon in iron. For the above reaction

$$K = \frac{p^2_{CO}}{p_{CO_2} \times a_c}$$

and any variation in the ratio $\frac{p^2_{CO}}{p_{CO_2} \times \%C}$ can be attributed to a variation in f_c, the activity coefficient of carbon. As can be seen from Table (3) this ratio is steadily increasing with increasing carbon content so that the activity coefficient of carbon must also be increasing. By plotting values of $\frac{p^2_{CO}}{p_{CO_2} \times \%C}$ against carbon content it is found by extrapolation that the value at zero carbon content is 426. Thus to obtain values of f_c the various values of $\frac{p^2_{CO}}{p_{CO_2} \times \%C}$ must be divided by 426. Values of f_c obtained in this way are shown

in column 4 of Table (3) and in column 5 are values of the activity of carbon on the dilute solution scale.

Table (3)

%C	$\frac{p^2_{CO}}{p_{CO_2}}$	$\frac{p^2_{CO}}{p_{CO_2} \times \%C}$	f_c	$a_c = f_c \times \%C$	a_c (pure scale)
0	-	426	1.00	0	0
0.216	93	430	1.00	0.216	0.0061
0.425	191	448	1.04	0.443	0.0125
0.64	292	455	1.06	0.68	0.0191
0.85	400	471	1.10	0.93	0.0261
1.06	525	495	1.16	1.23	0.0343
1.28	670	524	1.23	1.57	0.0438
1.68	1030	614	1.43	2.40	0.0673
2.10	1510	718	1.68	3.53	0.0988
2.50	2130	852	1.98	4.97	0.139
2.92	2930	1000	2.34	6.84	0.191
4.12	7200	1750	4.08	16.8	0.470
5.20	15300	2940	6.88	35.8	1.00

At 1546°C the solubility of carbon in iron is 5.20%. The activity of carbon in an alloy containing 5.20%C is thus unity on the pure scale. Activities on this scale at other compositions can then be obtained as

the ratio of any two activities is, of course, the same on either of the scales of measurement.

From purely theoretical considerations Temkin and Shvartsman[22] have obtained an equation for the activity of carbon in iron. This equation

$\gamma_c = \frac{1}{1 - 5 N_c}$, where γ_c is the activity coefficient and N_c is the atom fraction of carbon, has been derived on the assumption that the number of sites available to carbon in the iron lattice is equal to one fourth of the total number of iron atoms. The equation was derived in the first place for the activity of carbon in austenite but has also been applied to molten iron-carbon alloys. The activity co-efficient, γ_c, defined by the equation approaches unity as the atom fraction of carbon tends to zero. This coefficient is not strictly equal to $f_c \left(= \frac{a_c}{\%C}\right)$ but the relationship between thetwo coefficients can be calculated.

In the first case the activity is given by the equation

$$a_c = \gamma_c N_c$$

If the activity in the reference state (i.e. when $\gamma_c = 1$) be a_c' then

$$a_c' = N_c' \text{ where } N_c' \text{ is very small.}$$

In the second case if the activity in the reference state be

a''_C then

$$a''_C = \%C'' \text{ where } \%C'' \text{ is very small}$$

The ratio of the activity of carbon at any other carbon content to the activity in the reference state must be the same on each of the scales.

i.e. $$\frac{a_C}{a'_C} = \frac{a_C}{a''_C}$$

$$\frac{N_C \gamma_C}{N'_C} = \frac{f_C \%C}{\%C''}$$

Now $$N_C = \frac{\frac{\%C}{12}}{\frac{\%C}{12} + \frac{\%Fe}{56}} \cdot \frac{56 \times \%C}{56\%C + 12\% Fe}$$

and $$N'_C = \frac{56\%C''}{1200}$$ as $\%Fe \longrightarrow 100$ and $\%C \longrightarrow 0$.

Therefore $$\frac{N_C \gamma_C}{N'_C} = \frac{56 \times \%C}{56\%C + 12\% Fe} \cdot \gamma_C \cdot \frac{1200}{56 \times \%C''} = \frac{f_C \%C}{\%C''}$$

So that $$f_C = \gamma_C \cdot \frac{1200}{56\%C + 12\% Fe}$$

Values of the ratio $\frac{f_C}{\gamma_C}$ for various carbon contents are shown in Table (4) together with values of f_C calculated from Temkin and Shvartsman's [22] γ_C.

Table (4)

%C	$\frac{f_c}{\gamma_c}$	γ_c	f_c	f_c (Marshall and Chipman)
0.5	0.982	1.14	1.12	1.03
1.0	0.965	1.29	1.24	1.13
1.5	0.950	1.50	1.42	1.30
2.0	0.934	1.78	1.66	1.60
2.5	0.915	2.22	2.03	1.94
3.0	0.900	2.70	2.43	2.40
3.5	0.885	3.64	3.22	3.00
4.0	0.874	5.40	4.23	3.80
4.5	0.860	10.00	8.60	4.70

These values show good agreement with the experimental values of Marshall and Chipman[21] in the range 0-3.5%C. Above 3.5%C however, as $1-5N_c$ approaches zero the values calculated by Temkin and Shvartsman's equation rise rapidly with increasing carbon content. The two sets of values are shown graphically in Fig. (9) and where they diverge the values of Marshall and Chipman[21], being based on experiment, have been used in the present work for calculating the activity of carbon.

(ii) The effect of Silicon on the Activity Coefficient of Carbon

The effect of silicon on the activity coefficient of carbon can be calculated from the influence of silicon on the saturation carbon

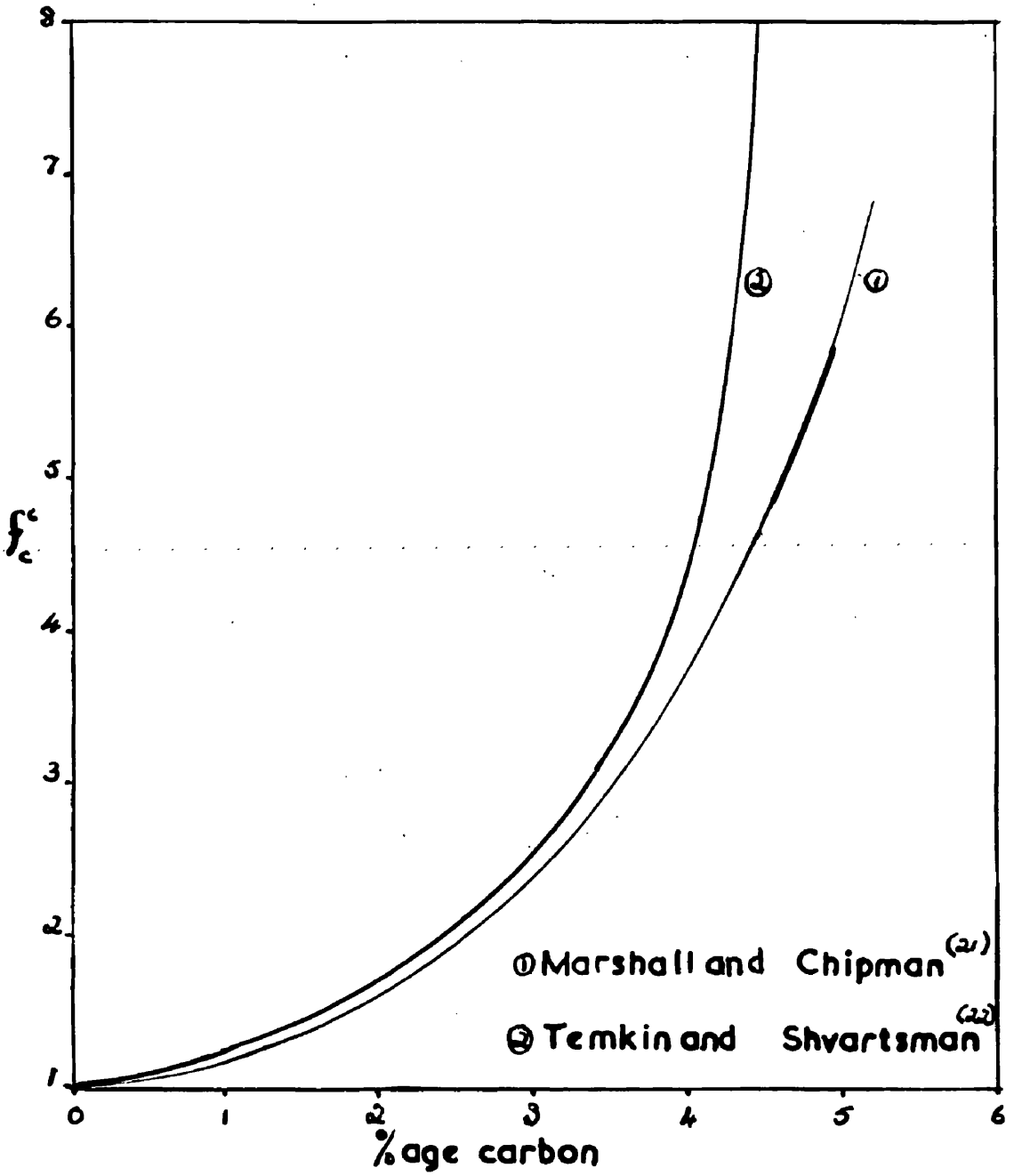


Fig. (9) Variation of the activity coefficient of carbon with carbon content (Fe-C alloys)

content of iron. The percentage carbon at saturation at 1500°C, obtained in the present work, is plotted as a function of silicon content in Fig. (10). Allowing for the effect of the small temperature difference these results are in good agreement with the values quoted by Chipman[13] for 1490°C. The effect of silicon on the activity coefficient of carbon can be calculated in the following way.

At 0% Si. the carbon content at saturation at 1500°C has been found in the present work to be 5.15%. The value of f_C^C found by Marshall and Chipman[21] for this carbon content is 6.6 so that the activity of carbon on the dilute solution scale is 34. At other silicon contents, as the metal was saturated with carbon, the activity of carbon must also be 34. Therefore by dividing 34 by the percentage carbon present, the activity coefficient of the carbon, f_C, in the iron carbon silicon alloys is obtained. The effect of silicon on the activity coefficient of carbon at saturation (f_C^{Si}) can then be calculated by dividing the values of f_C by the corresponding values of f_C^C, the activity coefficient in plain iron-carbon alloys. The values so obtained, in the range 0-12% Si, are shown in Table (5).

By assuming that the values of f_C^{Si} obtained at saturation are applicable at lower carbon contents the activity coefficient of carbon can be obtained for any composition in the ternary solution. In the present work an alternative method of calculating the activity coefficient at carbon contents other than saturation values has been developed. As the underlying principle of this method is the same as that used in calculating the activity of iron it will be discussed in the next section of this chapter.

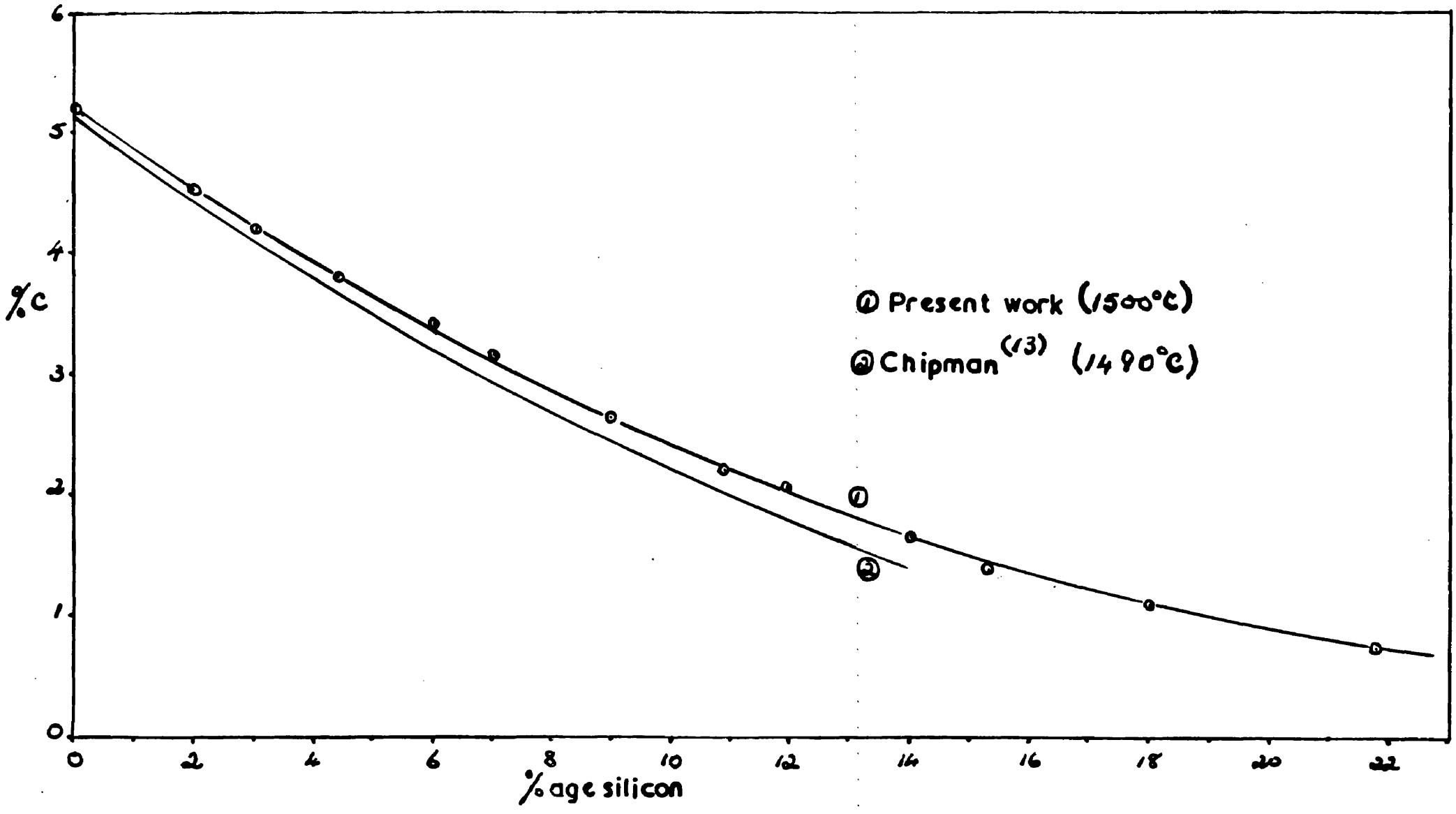


Fig. (10) Effect of silicon on the saturation carbon content of iron

Table (5)

% Si	%C	f_C^C	a_C	$f_C = \frac{a_C}{\%C}$	$f_C^{Si} = \frac{f_C}{f_C^C}$
0	5.15	6.60	34	6.60	1.0
1	4.85	5.50	34	7.01	1.27
2	4.50	4.70	34	7.55	1.61
3	4.20	4.15	34	8.10	1.95
4	3.90	3.65	34	8.72	2.39
5	3.65	3.25	34	9.32	2.87
6	3.40	2.90	34	10.0	3.45
7	3.10	2.50	34	10.9	4.36
12	2.0	1.6	34	17.0	10.60

On the assumption that the so called unit cell of iron cannot simultaneously contain both a silicon and a carbon atom, Samarin and Shvartsman[23] have extended Temkin and Shvartsman's[22] equation to iron-carbon-silicon alloys. The equation then becomes

$$\gamma_C = \frac{1}{1 - 5\,(N_C + N_{Si})}$$

where γ_C is the activity coefficient of carbon, N_C is the atom fraction of carbon and N_{Si} is the atom fraction of silicon. Values of the activity coefficient of carbon in iron-carbon-silicon alloys calculated by means of this equation agree well with the values obtained from the data on carbon saturation provided the carbon and silicon contents are low. At higher carbon and silicon percentages the values given by Samarin and Shvartsman's[23] equation are much higher. This is illustrated in Table (6).

Table (6)

%C	%Si	γ_c	f_c	f_c (from Marshall and Chipman plus carbon saturation results).
1	1	1.46	1.40	1.40
1	2	1.70	1.62	1.70
1	3	2.00	1.91	2.12
1	4	2.40	2.30	2.60
2	1	2.10	1.92	1.98
2	2	2.30	2.10	2.45
2	4	4.80	4.40	3.73
3	1	3.50	3.08	3,00
3	3	8.70	7.50	4.60
4	1	9.10	7.20	4.70
4	2	40.0	34.0	5.80

Samarin and Shvartsman's [23] equation implies that silicon and carbon are equivalent atom for atom in the liquid iron structure. This may be the case in dilute solutions but from a consideration of the data on the effect of silicon on carbon saturation it can be seen that it is not so in more concentrated solutions and herein probably lies the cause of the deviations of the calculated values of the activity coefficient from the experimental values. In Table (7) are shown the atom fractions of carbon and silicon in iron which is

saturated with carbon at 1500°C. The sum of these atom fractions increases with increasing silicon content. (fifth column of Table 7). This means that each atom of silicon entering the liquid structure displaces less than one atom of carbon i.e. one atom of silicon is equivalent to less than one atom of carbon.

Table (7)

% Si	% C	N_{Si}	N_C	$N_{Si} + N_C$
0	5.15	0	0.203	0.203
1	4.85	0.017	0.191	0.208
2	4.50	0.034	0.177	0.211
3	4.20	0.051	0.165	0.216
4	3.90	0.068	0.154	0.222
5	3.65	0.085	0.144	0.229
6	3.40	0.101	0.134	0.235
7	3.10	0.118	0.122	0.240
8	2.85	0.135	0.112	0.247
9	2.60	0.152	0.102	0.254
10	2.40	0.169	0.094	0.263

(d) Activity of Iron in Fe-C-Si Alloys

Although the activity of iron in iron-carbon and in iron-silicon solutions can be obtained by means of the Gibbs-Duhem equation it is

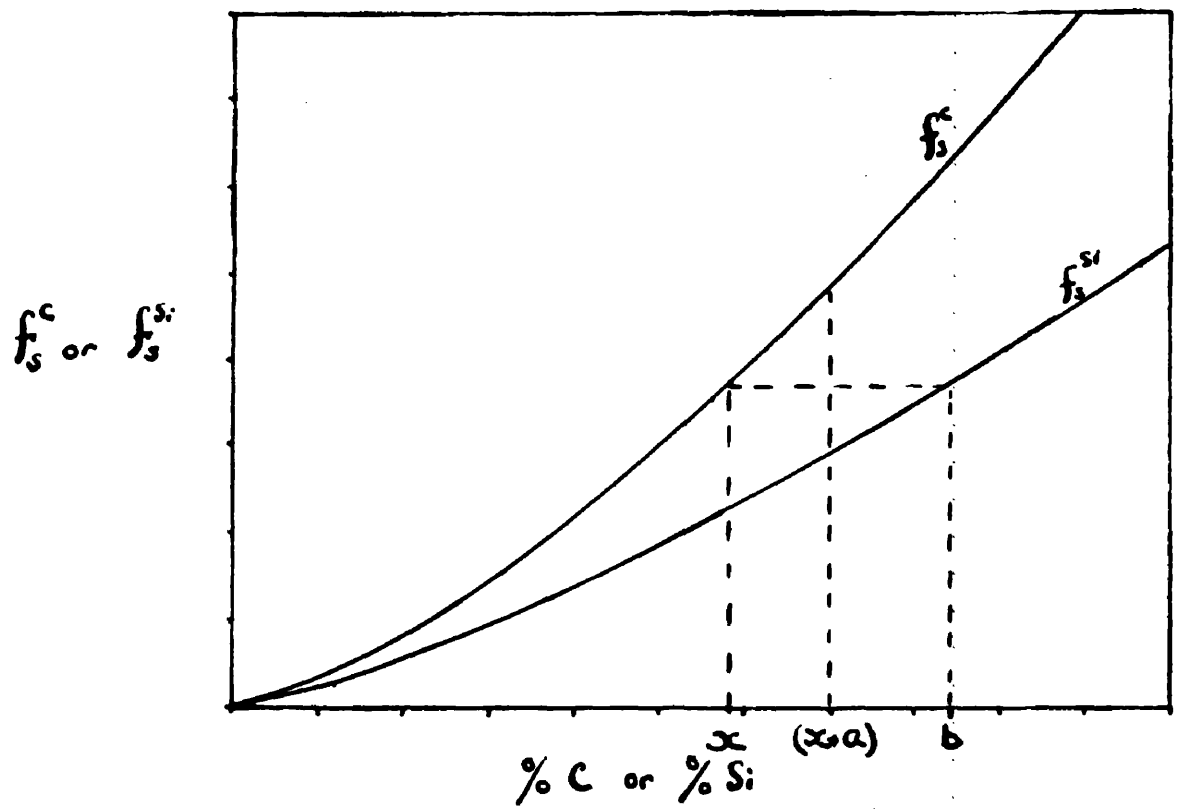
not possible to extend this equation in ternary iron-carbon-silicon alloys and as no experimental values are available some other method must be used in obtaining the activity of iron in such alloys. One method of doing this is by extending the line of thought of Morris and Buehl[24], Sherman and Chipman[25] and of Temkin, Samarin and Shvartsman[22] [23].

Morris and Buehl[24] in their study of the effect of carbon and silicon on the activity of sulphur in iron found that the activity coefficient of sulphur was not given by the equation

$$f_S = f_S^C \times f_S^{Si} \times f_S^S$$

where f_S is the activity coefficient of sulphur in the quaternary solution and f_S^C, f_S^{Si}, and f_S^S are the activity coeffieients in the Fe-C-S, Fe-Si-S and Fe-S solutions respectively. However by introduction the idea of the "carbon equivalent" of silicon the combined effect of carbon and silicon on the activity of sulphur could be calculated. The method employed is illustrated in Fig. (11). If the solution contained say a%C and b%Si then the effect of silicon on the activity coefficient of sulphur is the same as that of x% carbon. The combined effect of the carbon and silicon is then given by the value of f_S^C corresponding to (x + a) %C. Thus x% is the carbon equivalent of b%Si.

Sherman and Chipman[25] found that this method of combining activity coefficients was applicable in other quaternary solutions e.g. Fe-C-P-S and Fe-C-Mn-S and also in quinternary solutions e.g.



Fig(11) Method of combining activity coefficients as used by Morris and Buehl[24] and by Sherman and Chipman[25]

Fe-C-Al-Si-S. Although the method so far has only been used in finding the combined effect of two or more solutes on the activity coefficient of another it would seem probable that in certain cases the effect of two solutes on the activity of the solvent, may be estimated in a similar way.

This argument receives some support from the work of Samarin and Shvartsman[23] and of Temkin and Shvartsman[22]. Samarin and Shvartsman's [23] equation for the activity coefficient of carbon in Fe-C-Si alloys.

$$\gamma_C = \frac{1}{1 - 5\,(N_C + N_{Si})}$$

implies that, regarding their effect on the activity coefficient of carbon, carbon and silicon are equivalent atom for atom. Making the same basic assumption as Samarin and Shvartsman[23], i.e. that the number of places available to carbon in the iron lattice is equal to one fourth of the total number of iron atoms, Temkin and Shvartsman[22] have derived an equation for the activity of iron in iron-carbon alloys. This equation,

$$a_{Fe} = \left(\frac{N_{Fe} - 4\,N_C}{N_{Fe}}\right)^{\frac{1}{4}}$$

where a_{Fe} is the activity of iron on the pure scale and N_{Fe} and N_C are the atom fractions of iron and carbon respectively, gives, in the lower carbon range, values in excellent agreement with those calculated by Chipman[13] by means of the Gibbs-Duhem equation.

Table (8)

% C	0.85	2.10	4.12	4.50	5.00	5.20
a_{Fe} (T & S)	0.96	0.88	0.67	0.59.	0.34	0.0
a_{Fe} (Chipman)	0.96	0.88	0.70	0.66	0.61	0.59

At higher carbon contents (Table (8)) the two sets of values show considerable divergence probably because Temkin and Shvartsman's[22] basic assumption no longer holds. Although Temkin and Shvartsman did not apply their equation to liquid iron-carbon-silicon alloys it would be expected that an extended equation

$$a_{Fe} = \left(\frac{N_{Fe} - 4\,(N_C + N_{Si})}{N_{Fe}} \right)^{\frac{1}{4}}$$

would give, by analogy with the equation

$$\gamma_C = \frac{1}{1 - 5\,(N_C + N_{Si})}$$

accurate values of the activity of iron in dilute solutions but that in more concentrated solutions the activities of iron so obtained would diverge from the true values.

The principle remains, however, that if the silicon content can be replaced by a true "carbon equivalent" which is added to the carbon content then the effect of this total carbon represents the combined effect of carbon and silicon. Until the relationship between liquid metallic structure and activities is better understood the carbon

equivalent of silicon must be derived from experimental data.

One way of arriving at a carbon equivalent of silicon is by utilising the results on the effect of silicon on the saturation carbon content of iron at 1500°C. As explained in the previous section, values of f_c, the activity coefficient of carbon, can be derived from this data and these are reproduced in the third column of Table (9). In the first and second columns are the percentages of silicon and carbon at saturation.

Table (9)

%Si	%C	f_c	log f_c	Total Equivalent carbon	Carbon equivalent of silicon
0	5.15	6.60	0.8195	5.15	0
1	4.85	7.01	0.8457	5.25	0.40
2	4.50	7.55	0.8779	5.40	0.90
3	4.20	8.10	0.9085	5.55	1.35
4	3.90	8.72	0.9405	5.72	1.82
5	3.65	9.32	0.9694	5.85	2.20
6	3.40	10.0	1.000	6.00	2.60
7	3.10	10.9	1.0374	6.18	3.08

In Fig. (12) the values of log f_c obtained by Marshall and Chipman [21] in plain iron-carbon alloys are shown plotted against the percentage carbon. Log f_c is plotted rather than f_c to facilitate extrapolation

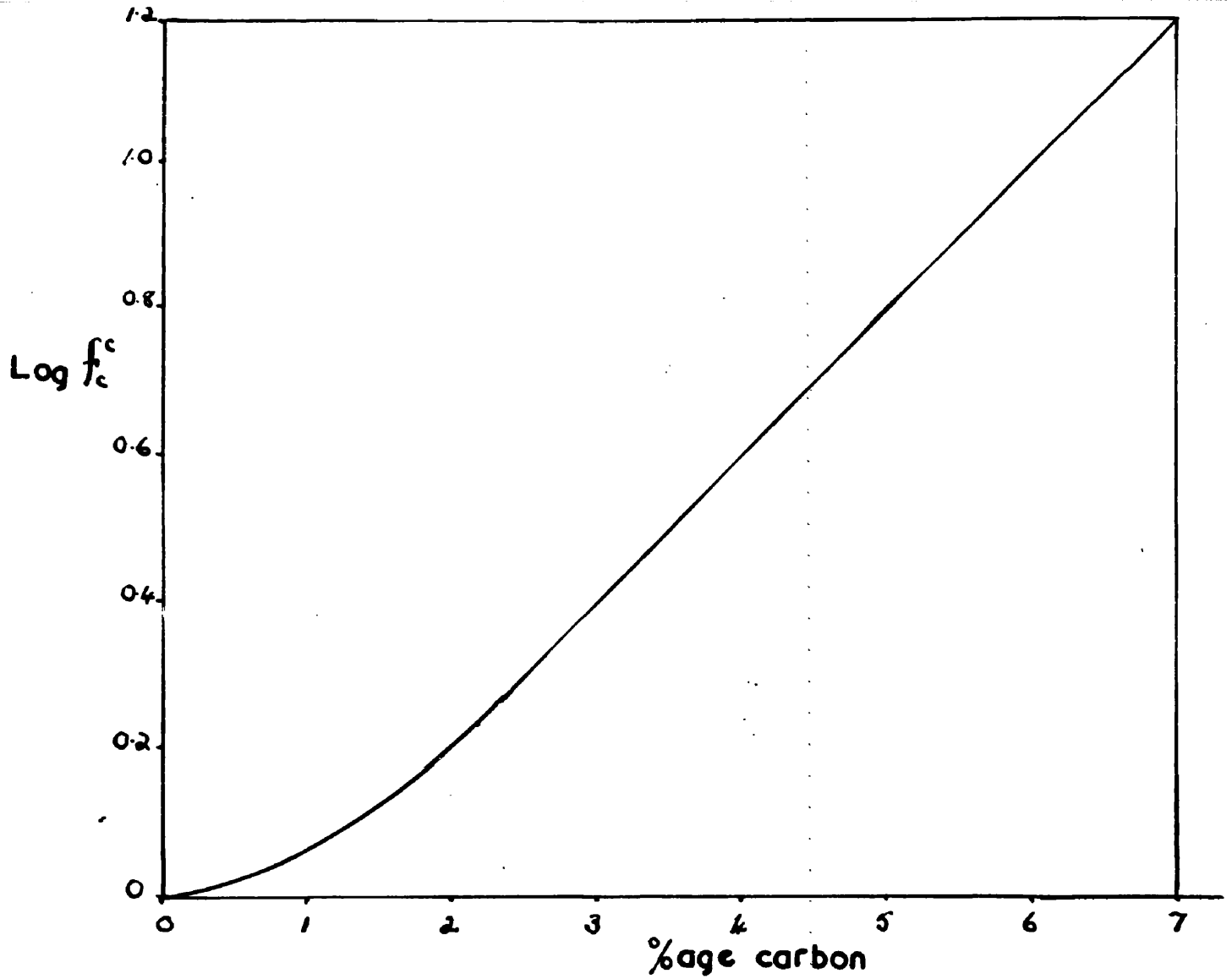


Fig. (12) Variation of Log f_c^c with percentage carbon

of the graph beyond carbon saturation. From the extrapolated portion of the line, carbon contents corresponding to the values of log f_C in Table (9) can be obtained and these are shown in the fifth column. These carbon contents represent the combined effects of carbon and silicon on the activity coefficient of carbon and by subtracting the actual carbon percentage present the carbon equivalent of silicon is obtained. These values are shown in the sixth column of Table (9) and also graphically in Fig. (13). Utilising this carbon equivalent of silicon the activities of iron and carbon at 1500°C can now be determined in iron-carbon-silicon alloys. Taking, for example, an alloy containing 3% carbon and 3% silicon,

the carbon equivalent of silicon from Fig. (13) = 1.35%

so that the total carbon content = 4.35%

From Fig. (11) log $f_C = 0.660$ and therefore $f_C = 4.57$. The activity of carbon is thus $4.57 \times 3 = 13.71$. Similarly, from Fig. (14) in which values of the activity of iron in plain iron carbon alloys, calculated by Chipman[13] by means of the Gibbs-Duhem equation, are plotted against percentage carbon, the activity of iron can be obtained. The value corresponding to 4.35% is 0.67.

For purposes of comparison, values of the activity of carbon calculated by this method are shown in Table (10) together with values calculated by the method indicated in the previous section.

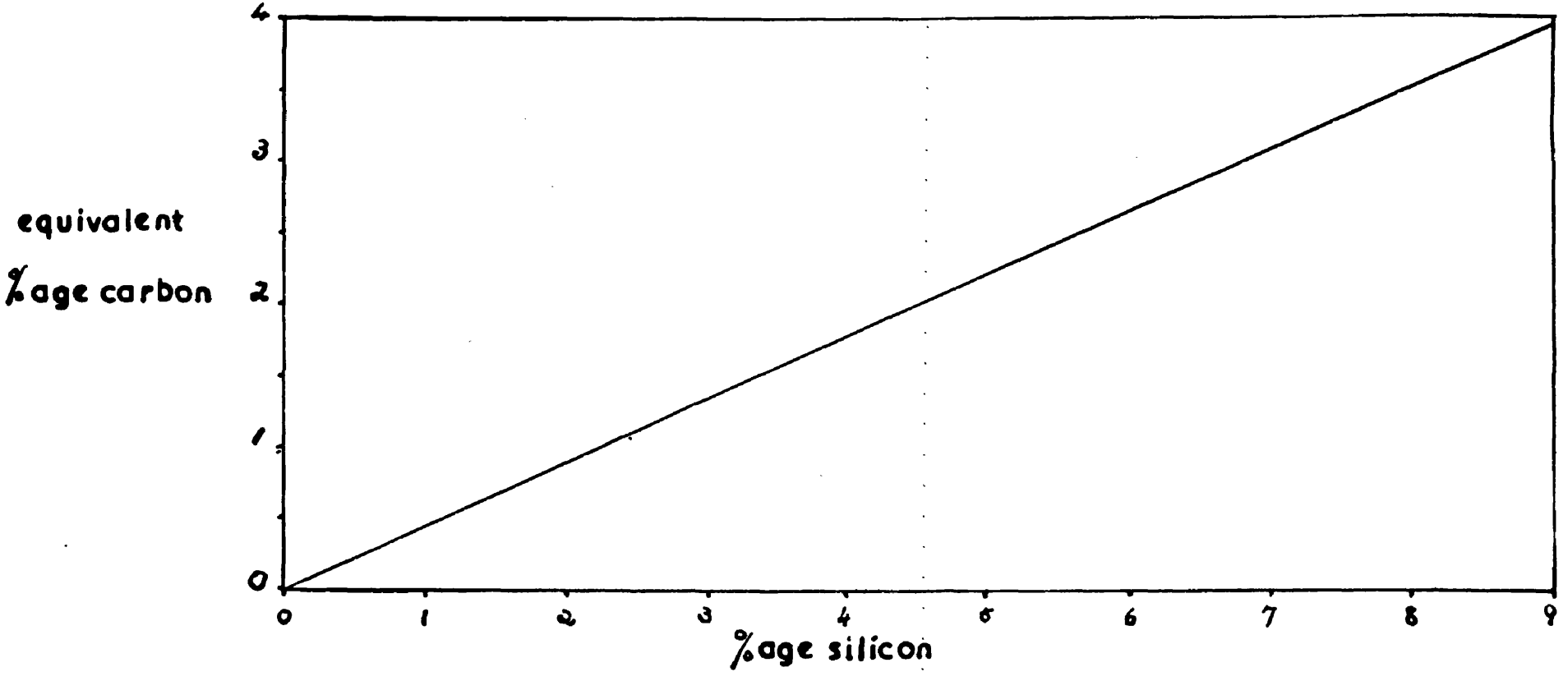


Fig. (13) Variation of the "equivalent carbon" with silicon content

Table(10)

% C	% Si	a_C ($= f_C^{Si} \times f_C^C \times \%C$)	Total equivalent carbon	a_C from equivalent carbon	a_{Fe} from equivalent carbon
1	1	1.32	1.45	1.32	0.92
1	2	1.69	1.90	1.55	0.89
1	4	2.48	2.80	2.22	0.82
2	1	4.08	2.45	3.90	0.85
2	2	5.18	2.90	4.62	0.81
2	4	7.70	3.80	7.00	0.73
3	1	9.15	3.45	9.00	0.76
3	4	17.25	4.80	16.35	0.63
4	1	19.32	4.45	18.60	0.67
4	2	24.44	4.90	22.80	0.62
4.5	1	27.5	4.95	26.6	0.61

In the sixth column of Table (10) are shown values of the activity of iron in the alloys selected. As can be seen the two sets of values of the activity of carbon differ but slightly. In the present work the values calculated from the equivalent carbon have been used because these do not require the assumption that the values of f_C^{Si} calculated at carbon saturation remain constant at lower carbon contents.

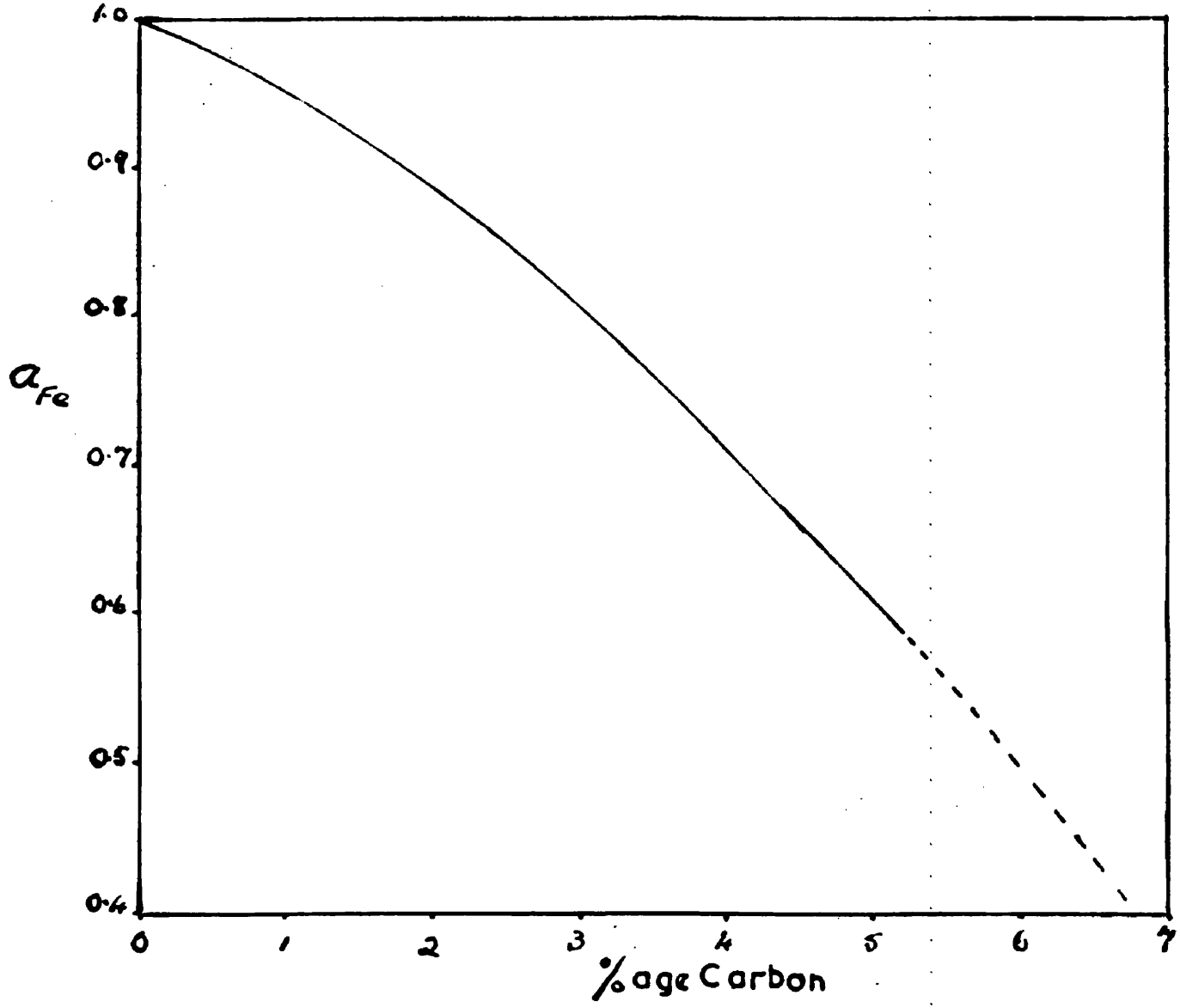


Fig. (14) Effect of carbon on the activity of iron

(e) The Activity of FeO

Taylor and Chipman[26] in their work on the activity of FeO in $CaO-MgO-SiO_2-FeO$ slags measured the activity of FeO in the range 90-10% FeO. Richardson and Jeffes[5] in a rather lengthy extrapolation from these results obtained a value of 0.03(referred to pure FeO) for a slag of this type containing 1% FeO.

Winkler and Chipman[27] in their study of the distribution of phosphorus between slag and metal also obtained values for the activity of FeO. They found in a complex slag mainly composed of CaO, SiO_2 and P_2O_5 but also containing small quantities of CaF_2 and MnO that for an FeO content of approximately 3% the activity of FeO was 0.10. Assuming that in the range 1~3% FeO the activity of FeO is proportional to the percentage FeO then 1% FeO would correspond to an activity of 0.033.

Although these two results are in substantial agreement it is thought that, in view of the large difference in composition between these basic slags and slags of the blast furnace type, the application of these activity figures to the latter type of slag is hardly justified.

(f) The Activity of SiO_2 in $CaO \sim Al_2O_3 - SiO_2$ Slags.

Several investigators[20] [28] have computed, from the phase diagram, the activity of silica at 1600°C in $CaO-SiO_2$ melts. The various values obtained are in substantial agreement and those of Rey[28] are shown in Fig. (15). Chang and Derge[29] determined the

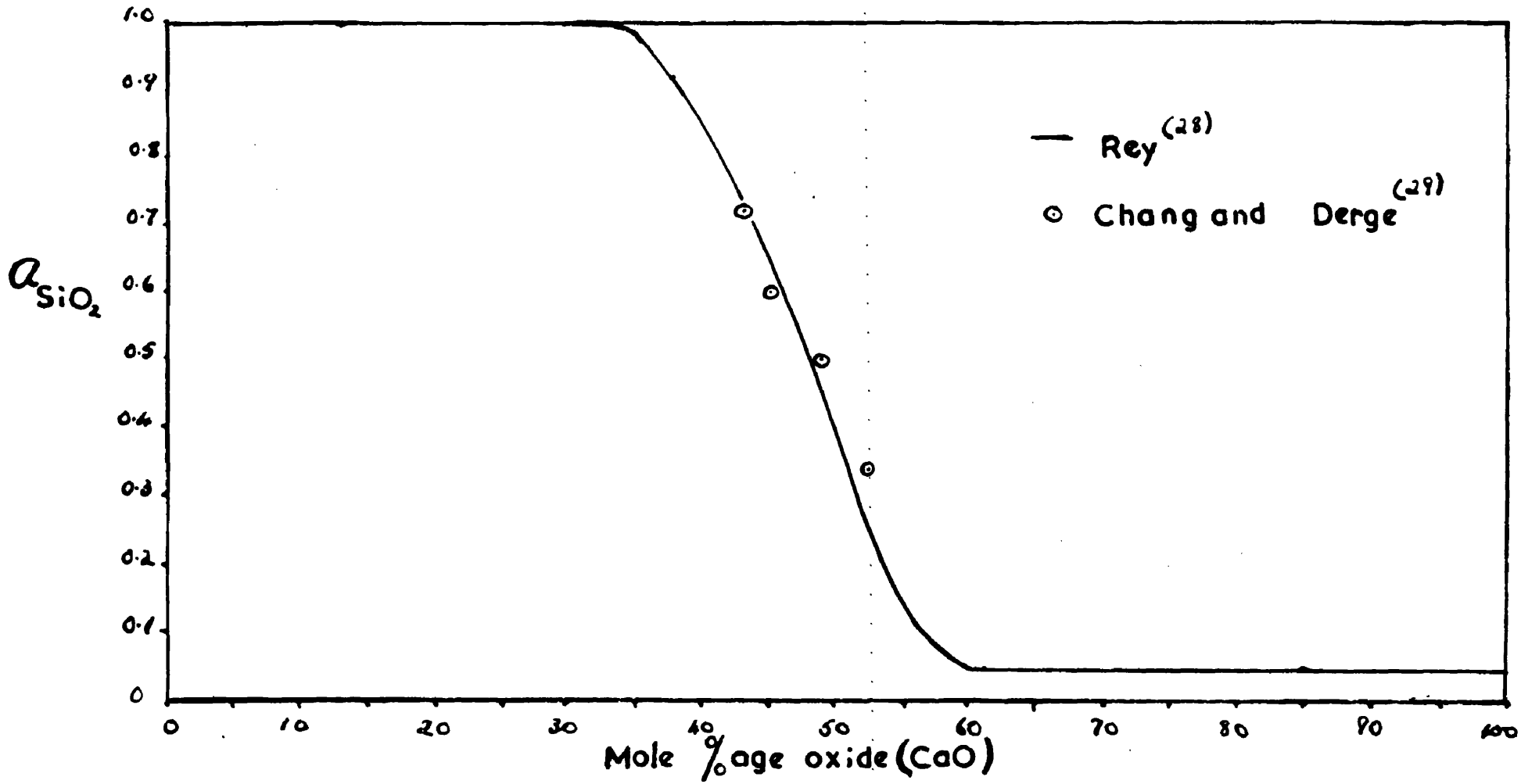


Fig.(15) Activity of silica in lime-silica system

activity of silica in molten calcium silicates using an electromotive force method in which the two electrodes were graphite and silicon carbide. Their results, shown in Fig. (15) are in good agreement with those calculated from the phase diagram. Chang and Derge also made some measurements in the $CaO\sim Al_2O_3\sim SiO_2$ system but, in this case, although the activities of silica in the various melts could be calculated relative to one another, the values could not be placed on an absolute scale, i.e. on a scale relative to pure silica at 1600°C.

Fulton, Grant and Chipman[3] in a recent paper studied the equilibrium position of the reaction

$$(SiO_2) + 2C = \underline{Si} + 2CO \text{ at } 1600^\circ C$$

The equilibrium constant for this reaction is

$$K = \frac{a_{Si} \times p^2_{CO}}{a_{SiO_2} \times a^2_C}$$

As the work was carried out in graphite crucibles under a CO pressure of one atmosphere $a_C = p_{CO} = 1$, so that

$$K = \frac{a_{Si}}{a_{SiO_2}}$$

In each case the metal was saturated with carbon so that alloys with equal silicon contents had equal silicon activities and therefore the slags in contact with these metals had equal silica activities.

Fig. (16) reproduced from Fulton, Grant and Chipman's paper shows iso-silicon and therefore iso-silica activity lines. Although the actual silica activities corresponding to the various percentages of silicon were not calculated in the original paper, this can be done using the results of Rey[28] (Fig. (15)). For example 20% Si is obtained at equilibrium under a plain $CaO-SiO_2$ slag containing 54% CaO. This corresponds to a molar percentage lime of 55.7 and an activity of silica from Rey's curve of 0.14. The values of the activity of silica, calculated in this way, for the other iso-silicon lines are marked in Fig. (16).

The slag used in the present work had the composition 31% CaO, 28% SiO_2, 41% Al_2O_3 and is marked by a cross in Fig. (16). As can be seen it lies well outside the range of composition covered by the work of Fulton, Grant and Chipman[3] and extrapolation of the iso-silica activity lines is not justified.

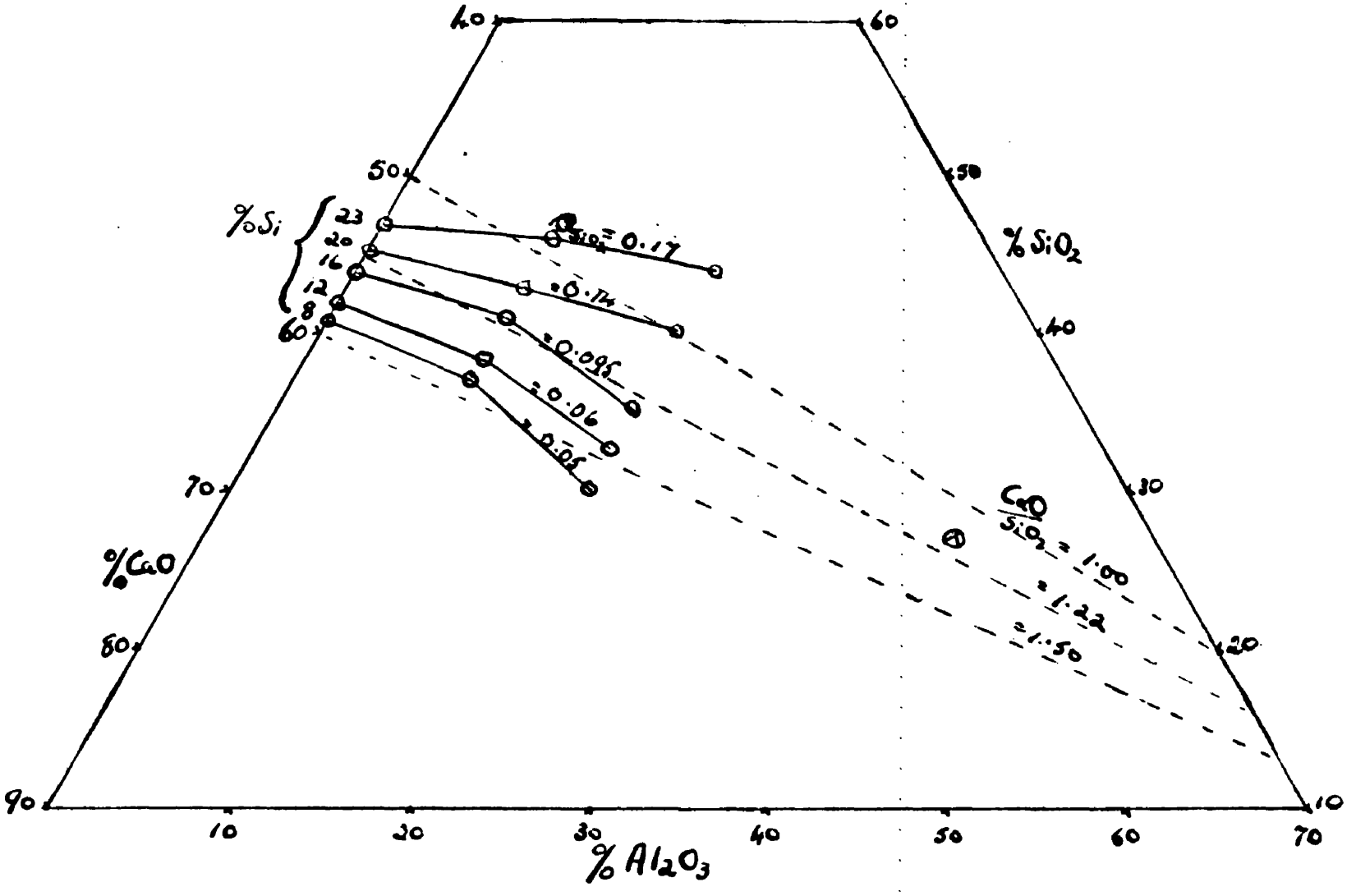


Fig.(16) Activity of silica in lime-alumina-silica system

5. DISCUSSION OF RESULTS.

(a) Introduction.

The reactions which have been studied in the present work are

(1) $\underline{C} + (FeO) = CO + \underline{Fe}$

(2) $\underline{Si} + 2\,(FeO) = (SiO_2) + 2\,\underline{Fe}$

(3) $2C + (SiO_2) = \underline{Si} + 2CO$

The experiments performed in the study of the first two reactions and in which FeO was present in the slag were carried out in the composite molybdenum alumina crucibles described in Chapter (3). In the study of the third reaction the metal and slag were contained in graphite crucibles.

In Table (11) are presented the chemical analyses of samples of metal and slag from the experiments performed at 1500°C in the investigation of the equilibrium positions of reactions (1) and (2). The results obtained in the study of reaction (3) will be discussed in a later section of this chapter.

The equilibrium constants for reactions (1) and (2) are

$$K'_c = \frac{p_{CO} \times a_{Fe}}{a_C \times a_{FeO}} \quad \text{and} \quad K'_{Si} = \frac{a_{SiO_2} \times a^2_{Fe}}{a_{Si} \times a^2_{FeO}}$$

where the symbols are as defined in the previous chapter. To facilitate discussion of the results, the reciprocals of these equilibrium constants, denoted by K_c and K_{Si} respectively have been used.

Table (11)

Run A	Time at 1500°C	Metal		Slag			
		Si	C	FeO	CaO	Al_2O_3	SiO_2
	Hrs.						
11	4½	0.20	3.50	1.40	30.5	41.4	28.1
12	4½	0.67	3.82	0.68	29.5	41.5	28.0
13	4	0.85	3.42	0.90	29.6	42.0	27.7
14	4½	0.95	3.40	0.88	-	-	27.4
15	4½	1.07	3.57	0.90	30.0	41.0	27.2
16	4½	1.21	3.72	0.55	30.5	-	27.0
17	4	1.41	3.47	0.99	31.1	-	28.3
18	4	1.79	3.30	1.08	29.2	40.5	27.5
19	4	2.25	3.50	0.76	29.3	42.0	27.9
20	4½	2.28	3.34	0.79	30.3	-	29.0
21	4½	2.32	3.43	0.86	30.7	41.0	28.0
22	4½	2.40	3.16	0.86	30.0	41.0	27.1
23	4½	2.45	3.27	0.80	31.0	41.0	28.3
24	4½	3.28	2.87	0.76	30.2	41.3	27.1
25	4	3.92	3.27	0.50	30.5	41.0	27.9
26	4	3.97	3.26	0.43	30.1	-	27.7
27	4½	3.98	3.24	0.42	31.5	39.8	28.4
28	4	5.10	2.52	0.35	30.1	42.0	27.1
29	4½	5.50	2.46	0.32	-	-	27.5
30	4	0.68	2.66	1.15	30.4	-	27.3
31	4	0.76	2.86	1.00	29.7	-	28.0
32	4	5.54	1.61	0.33	31.5	41.0	28.2
33	4½	0.05	4.30	0.45	30.2	-	28.0
34	4	0.05	3.87	0.85	31.2	-	27.1
35	4	0.05	3.50	1.18	30.5	-	27.2

(b) (i) The reaction $\underline{C} + (FeO) = CO + Fe$

As the partial pressure of carbon monoxide could be taken as unity as explained in Chapter (3), the equilibrium constant for this reaction becomes

$$K_c = \frac{a_C \times a_{FeO}}{a_{Fe}}$$

In Table (12) are shown values of the activities of carbon and of iron calculated by the method involving the carbon equivalent of silicon as explained in the previous chapter. As no value is available for the activity of FeO in such slag it was assumed as a first approximation, that the activity of FeO is proportional to the percentage. Values of $'K_c$ using the activities so calculated are also presented in Table (12). In the three runs A30, A31, and A32, the metal was not initially saturated with carbon and as no carbon drop occurred on the addition of FeO it was assumed that the carbon content was lower than that in equilibrium with the FeO added. As no mechanism was available by which the carbon content could increase these runs could not come to equilibrium with respect to carbon and for this reason values of $'K_c$ have not been calculated.

In the runs, A33, A34, and A35, no silicon was added to the initial metal so that the effect of silicon on the activities of carbon and iron could be eliminated.

As can be seen from Table (12) and Fig. (17) the values of $'K_c$ are not constant and show a tendency to increase with increasing

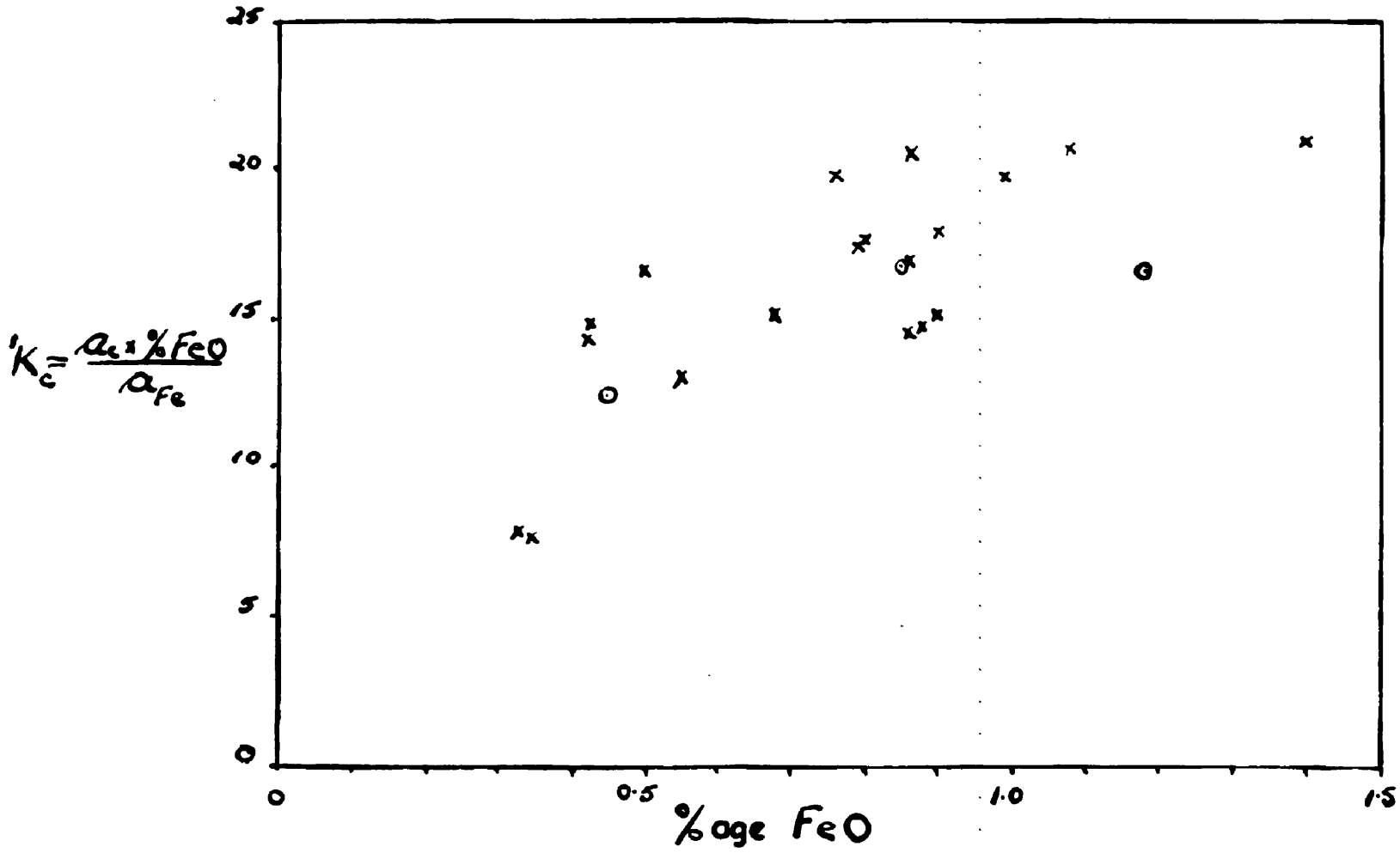


Fig.(17) Variation of $'K_c = \frac{a_c \times \%FeO}{a_{Fe}}$ with percentage FeO

Table (12)

Run A	% Si	% C	%FeO	≡ C	"Total" C	a_{Fe}	f_C	a_c	$'K_C \times 10^{-1}$
11	0.20	3.50	1.40	0.10	3.60	0.76	3.25	11.4	2.10
12	0.67	3.82	0.68	0.30	4.12	0.70	4.10	15.5	1.51
13	0.85	3.42	0.90	0.38	3.80	0.73	3.60	12.3	1.51
14	0.95	3.40	0.88	0.43	3.83	0.73	3.60	12.2	1.47
15	1.07	3.57	0.90	0.47	4.04	0.70	4.0	14.1	1.80
16	1.21	3.72	0.55	0.53	4.25	0.69	4.40	16.4	1.31
17	1.41	3.47	0.99	0.62	4.09	0.70	4.05	14.0	1.98
18	1.79	3.30	1.08	0.78	4.08	0.70	4.05	13.4	2.07
19	2.25	3.50	0.76	L.00	4.50	0.66	4.90	17.1	1.97
20	2.28	3.34	0.79	1.02	4.34	0.68	4.50	15.0	1.74
21	2.32	3.43	0.86	1.02	4.45	0.67	4.70	16.0	2.06
22	2.40	3.16	0.86	1.06	4.22	0.69	4.30	13.6	1.69
23	2.45	3.27	0.80	1.10	4.37	0.68	4.57	15.0	1.76
24	3.28	2.87	0.76	1.45	4.32	0.68	4.50	12.9	1.44
25	3.92	3.27	0.5o	1.73	5.00	0.61	6.20	20.3	1.66
26	3.97	3.26	0.43	1.78	5.04	0.60	6.30	20.5	1.47
27	3.98	3.24	0.42	1.79	5.03	0.60	6.30	20.5	1.44
28	5.10	2.52	0.35	2.25	4.77	0.64	5.50	13.9	0.76
29	5.50	2.46	0.32	2.43	4.89	0.62	6.00	14.8	0.77
30	0.68	2.66	1.15	0.30	2.96	0.81	2.40	6.40	-
31	0.76	2.86	1.00	0.35	3.21	0.78	2.66	7.60	-
32	5.54	1.61	0.33	2.47	4.08	0.71	4.07	6.55	-
33	0.05	4.30	0.45	-	4.30	0.68	4.35	18.70	1.24
34	0.05	3.87	0.85	-	3.87	0.72	3.65	14.10	1.67
35	0.05	3.50	1.18	-	3.50	0.76	3.05	10.70	1.66

≡ C = equivalent carbon

percentage of FeO. This would indicate that the activity of FeO is not proportional to the percentage but that the activity coefficient $\left(= \frac{a_{FeO}}{\%FeO}\right)$ is decreasing with increasing percentage of FeO.

(ii) Calculation of the Activity of FeO

From a consideration of the equation $K_c = \frac{a_c \times a_{FeO}}{a_{Fe} \times p_{co}}$ it can be seen that $a_{FeO} = K_c \times \frac{a_{Fe}}{a_c}$ when $p_{co} = 1$. From the thermodynamic data given by Richardson and Jeffes[18] the value of K_c can be calculated.

Thus

(i) $Fe + \frac{1}{2}O_2 = FeO$ $\quad \Delta G^\circ = -55,625 + 10.84T$

(ii) $C + \frac{1}{2}O_2 = CO$ $\quad \Delta G^\circ = -26,700 \ -20.95T$

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and by subtraction

(iii) $Fe + CO = C + FeO$ $\quad \Delta G^\circ = -28,925 + 31.79T$

Therefore at 1500°C, $-RT \log_e K_c = 27,575$ cals and

$$K_c = 4.07 \times 10^{-4}$$

The free energy expression for reaction (ii) refers, to the oxidation of graphite and not to carbon dissolved in iron so that the value of K_c obtained incorporates the activity of carbon measured on the pure scale. The activity of carbon in iron saturated with carbon at 1500°C is, on the pure scale, unity, and on the dilute solution scale, 34 (5.15 x 6.6). By dividing by 34, the activities of carbon in

Table (12) have thus been converted to the pure scale and values of $K_c \times \frac{a_{Fe}}{a_c}$ are shown plotted against the percentage of FeO in Fig. (18). The three runs in which there was no silicon present are marked thus ⊙. The mean line has been drawn through these points as it was thought that the activities of iron and carbon in plain iron carbon alloys are more firmly established than those in Fe-C-Si solutions. The remaining points are grouped fairly closely round this line but the fact that the majority of the points lie below the line would suggest that there is some small systematic error which results in either an under estimated activity of iron or an over estimated activity of carbon.

The values of the activity of FeO, on the pure scale, for various percentages of FeO are presented in Table (13). Also shown in the Table are two activity coefficients; one equal to the activity divided by the percentage of FeO and the other the normal activity coefficient, γ, equal to the activity divided by the mole fraction.

Table (13)

%FeO	0.3	0.5	0.7	0.9	1.1	1.3	1.4
$a_{FeO} \times 10^4$	3.9	5.2	6.5	7.8	9.0	10.3	11.0
$\frac{a_{FeO}}{\%FeO} \times 10^4$	13.0	10.4	9.3	8.7	8.2	7.9	7.8
$\frac{a_{FeO}}{N_{FeO}}$	0.13	0.11	0.10	0.09	0.084	0.082	0.081

The results show that FeO when dissolved in the slag of the composition used in these experiments exhibits strong negative deviations from

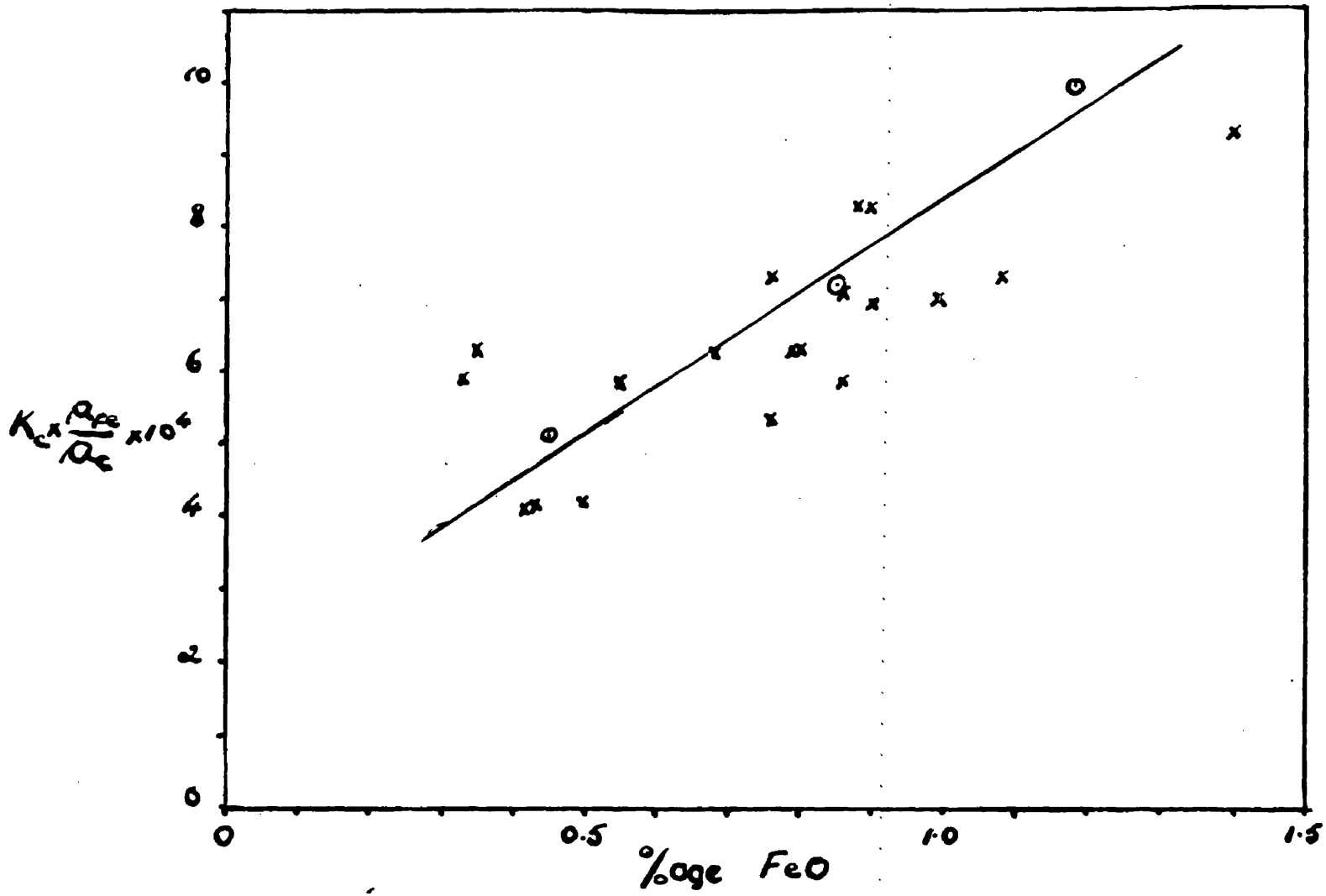

Fig.(18) Variation of $K_c \times \frac{a_{Fe}}{a_c} \times a_{FeO}$ with percentage FeO

ideal behaviour. The value of the activity corresponding to 1% FeO is approximately 30 times smaller than the value of 0.03 calculated by Richardson and Jeffes[5] from the results of Taylor and Chipman[26] on more basic slags. A surprising feature of the results is the fact that γ_{FeO} decreases by a factor of 2 in the small range of FeO contents examined. In view of the major influence which the slag FeO exerts on the sulphur and silicon contents of pig iron it would be desirable to know whether the above effects are due to the high alumina content of the slag used in the experiments or whether they are found in more normal blast furnace type slags.

(c) The Reaction $Si + 2\ FeO = SiO_2 + 2\ Fe$

For the above reaction, the equilibrium constant used in the present work is given by the equation

$$K_{Si} = \frac{a_{Si} \times a^2_{FeO}}{a_{SiO_2} \times a^2_{Fe}}.$$

It can be seen, however, from Table (11) that apart from the FeO content, the percentage variation in the other slag constituents is very small and for this reason the activity of silica has been taken as being constant throughout the series of experiments. The product $\frac{a^2_{FeO} \times a_{Si}}{a^2_{Fe}}$ should therefore be constant and this product has been denoted by $'K_{Si}$. In Table (14) are shown values of the activities of silicon and iron calculated as indicated in Chapter (4). Two sets of values for the activity of silicon are shown, the first set

Table (14)

Run A	% Si	% C	% FeO	f^{Si}_{Si}	f^{*Si}_{Si}	f^{C}_{Si}	a_{Si}	a^{*}_{Si}	a_{Fe}	$^{2}K_{Si}$	$^{2}K^{*}_{Si}$
11	0.20	3.50	1.40	1.10	1.01	3.35	0.74	0.68	0.76	2.51	2.16
12	0.67	3.82	0.68	1.33	1.02	3.75	3.32	2.55	0.70	3.13	2.40
13	0.85	3.42	0.90	1.41	1.03	3.25	3.90	2.84	0.73	5.60	4.15
14	0.95	3.40	0.88	1.45	1.04	3.25	4.47	3.21	0.73	6.50	4.65
15	1.07	3.57	0.90	1.51	1.04	3.45	5.55	3.85	0.70	9.15	6.30
16	1.21	3.72	0.55	1.59	1.05	3.62	7.00	4.60	0.68	4.60	3.03
17	1.41	3.47	0.99	1.66	1.06	3.32	7.75	4.95	0.70	15.8	10.10
18	1.79	3.30	1.08	1.82	1.07	3.15	10.3	6.05	0.70	24.5	14.4
19	2.25	3.50	0.76	2.00	1.08	3.35	15.1	8.15	0.64	19.7	10.8
20	2.28	3.34	0.79	2.01	1.08	3.15	14.4	7.75	0.67	19.9	10.7
21	2.32	3.43	0.86	2.02	1.08	3.25	15.3	8.15	0.66	26.0	13.9
22	2.40	3.16	0.86	2.04	1.08	3.00	14.7	7.76	0.68	23.5	12.4
23	2.45	3.27	0.80	2.06	1.09	3.10	19.7	8.30	0.67	28.0	11.8
24	3.28	2.87	0.76	2.40	1.12	2.70	21.2	9.90	0.67	25.0	11.7
25	3.92	3.27	0.50	2.63	1.14	3.10	32.0	13.8	0.60	22.2	9.90
26	3.97	3.26	0.43	2.64	1.14	3.10	32.3	14.0	0.60	16.6	7.20
27	3.98	3.24	0.42	2.65	1.14	3.10	32.2	14.1	0.60	15.8	6.80
28	5.10	2.52	0.35	2.92	1.18	2.40	35.6	14.4	0.62	11.5	4.65
29	5.50	2.46	0.32	3.02	1.20	2.30	38.8	15.2	0.60	11.0	4.35
30	0.68	2.66	1.15	1.33	1.02	2.50	2.28	1.74	0.81	4.55	3.50
31	0.76	2.86	1.00	1.37	1.02	2.70	2.77	2.10	0.78	4.55	3.44
32	5.54	1.61	0.33	3.02	1.20	1.75	29.2	11.6	0.69	6.75	2.68

being obtained using the values of f_{Si}^{Si} given by Chipman[13] and the second set using the values of f_{Si}^{Si} given by Gokcen and Chipman[12]. In both cases the values of f_{Si}^{C} obtained by Chipman[13] from Körbers[18] results have been used. Where Chipman's[13] values of f_{Si}^{Si} have been used the activity of silicon has been marked with an asterisk thus a_{Si}^{*} and values of K_{Si} obtained using this activity of silicon have been similarly marked.

In the first case the activity of FeO has been taken as being proportional to the percentage and values of $^{2}K_{Si}$ and $^{2}K_{Si}^{*}$ $\left({}^{2}K_{Si} = \frac{a_{Si} \times (\%FeO)^2}{a^2_{Fe}} \right)$ are shown in Table (14). As can be seen these are not constant and when plotted against the percentage of silicon give the curves shown in Figs. (19) and(20). By replacing the percentages of FeO by the activities found from the carbon results values of $'K_{Si}$ and $'K_{Si}^{*}$ are obtained and these exhibit equally large variations Table (15).

In an attempt to determine which activity is in error the activities of FeO and iron have been eliminated in the following way.

$$K_{Si} = \frac{a_{Si} \times a^2_{FeO}}{a^2_{Fe} \times a_{SiO_2}} \qquad \text{and } K_C = \frac{a_C \times a_{FeO}}{a_{Fe}}$$

Therefore $$\frac{K_C^2}{K_{Si}} = \frac{a^2_C}{a_{Si}} \times a_{SiO_2}$$

i.e. when the activity of silica is constant the ratio $\frac{a^2_C}{a_{Si}}$ should also be constant. The values of K_{Si} can be determined from thermodynamic data in a similar way to that employed in calculating K_C

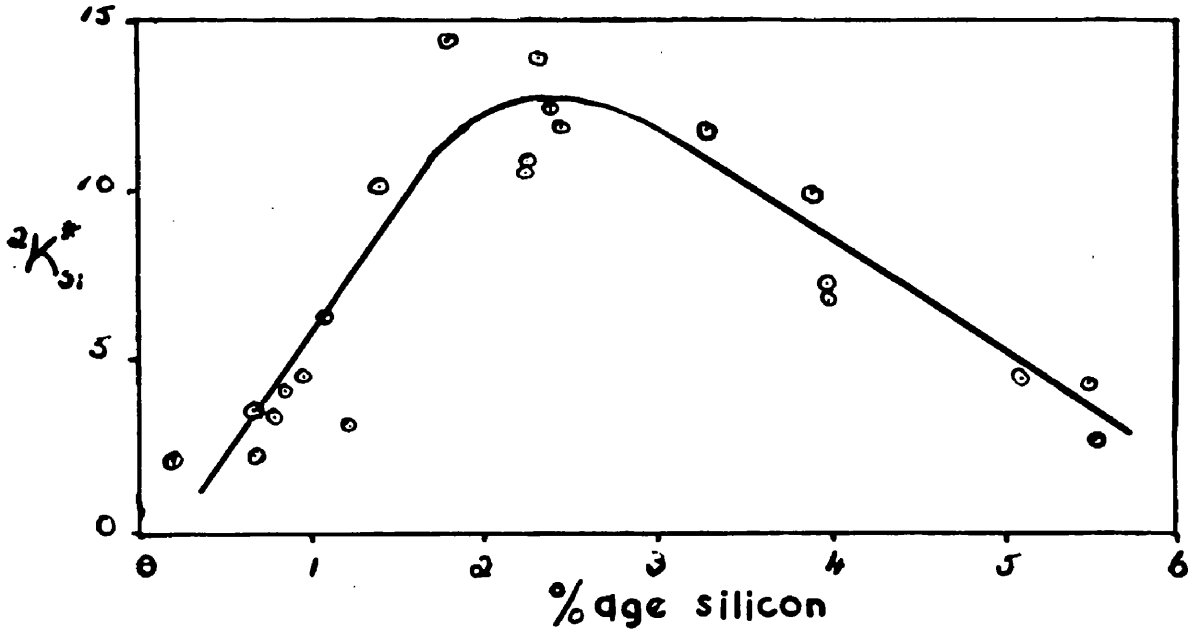

Fig.(19) Variation of $^2K^*_{Si}$ with percentage silicon

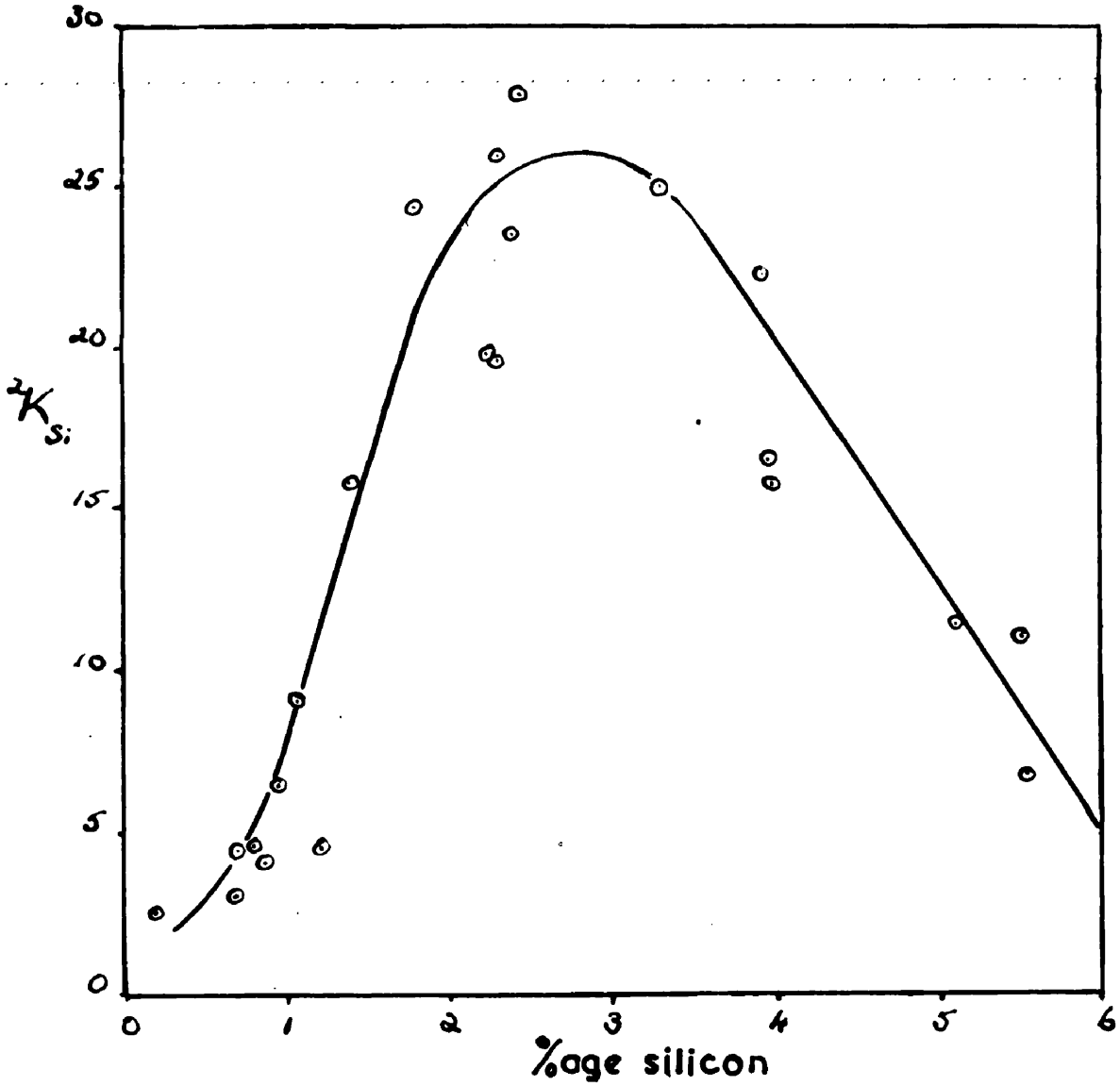

Fig.(20) Variation of $^2K_{Si}$ with percentage silicon

Table (15)

A	$'K_{Si} \times 10^6$	$'K^{*}_{Si} \times 10^6$
11	1.52	1.39
12	2.69	2.06
13	4.34	3.15
14	4.87	3.50
15	6.70	4.65
16	4.47	2.94
17	11.20	7.14
18	16.40	9.60
19	16.20	8.71
20	15.40	8.32
21	18.70	9.95
22	16.90	8.90
23	21.50	9.05
24	21.2	9.90
25	23.4	10.1
26	20.4	8.82
27	20.3	8.90
28	15.7	6.35
29	17.1	6.70
30	3.20	2.32
31	3.22	2.44
32	9.60	3.83

i.e.

$2Fe + O_2 = 2FeO$ $\quad \Delta G^\circ = -111,250 + 21.67T$

$Si_{(l)} + O_2 = SiO_2$ $\quad \Delta G^\circ = -217,600 + 48.79T$

$2Fe + SiO_2 = Si_{(l)} + 2FeO$ $\quad \Delta G^\circ = 106,350 - 27.12T$

$+ 58,400$ cals. at $1500^\circ C$

$Si_{(l)} = Si_{(\text{in Fe})}$ $\quad \Delta G^\circ$ $-27,200$ cals. at $1500^\circ C$

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so that $2Fe + SiO_2 = Si_{(\text{in Fe})} + 2\,FeO$ $\quad \Delta G^\circ = +31,200$

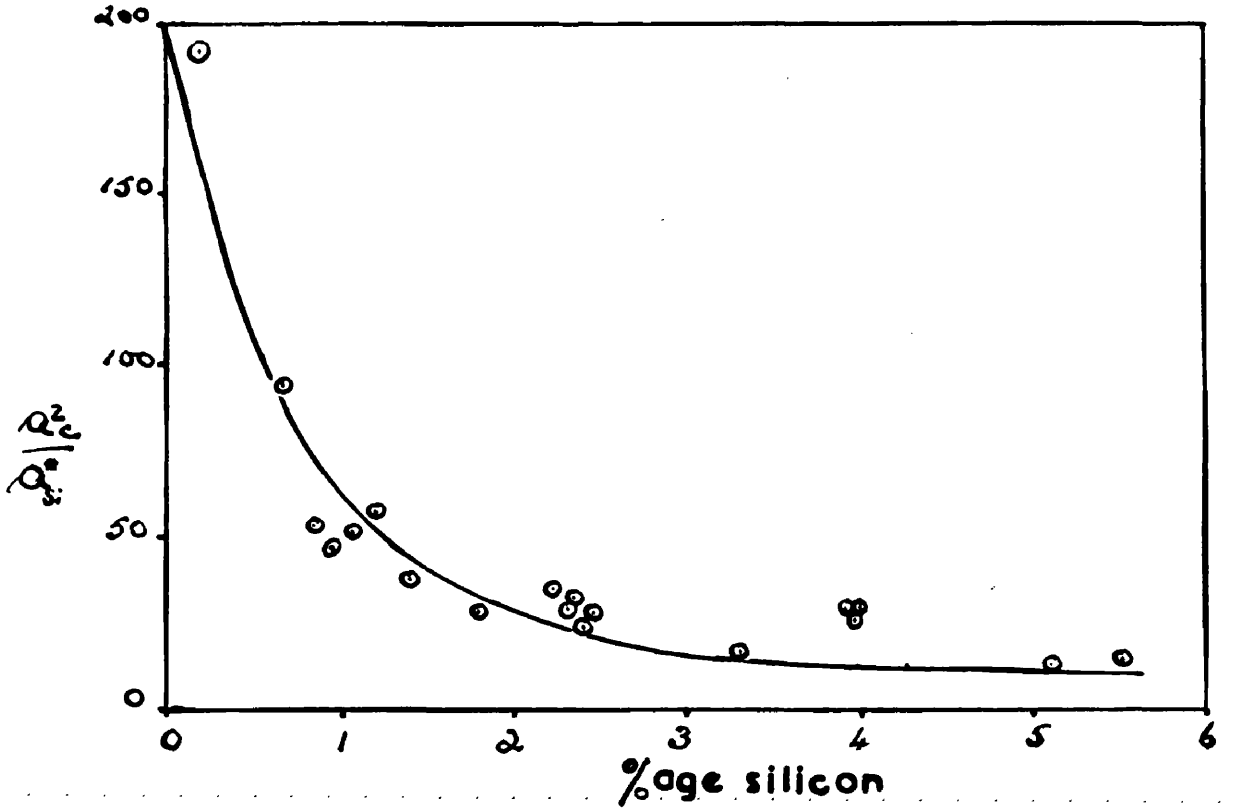
or $K_{Si} = 1.41 \times 10^{-4}$

K_c has been previously calculated as 4.07×10^{-4} when the activity of carbon is on the pure scale. The corresponding value when a_c is on the dilute solution scale is $4.07 \times 10^{-4} \times 34 = 1.39 \times 10^{-2}$. The ratio $\frac{a_c^2 \times a_{SiO_2}}{a_{Si}}$ should thus be equal to 1.37. The value of the activity of silica has been estimated from the results of experiments done in carbon crucibles as being 0.16 (p. 80) and inserting this value we have $\frac{a_c^2}{a_{Si}} = 8.5$.

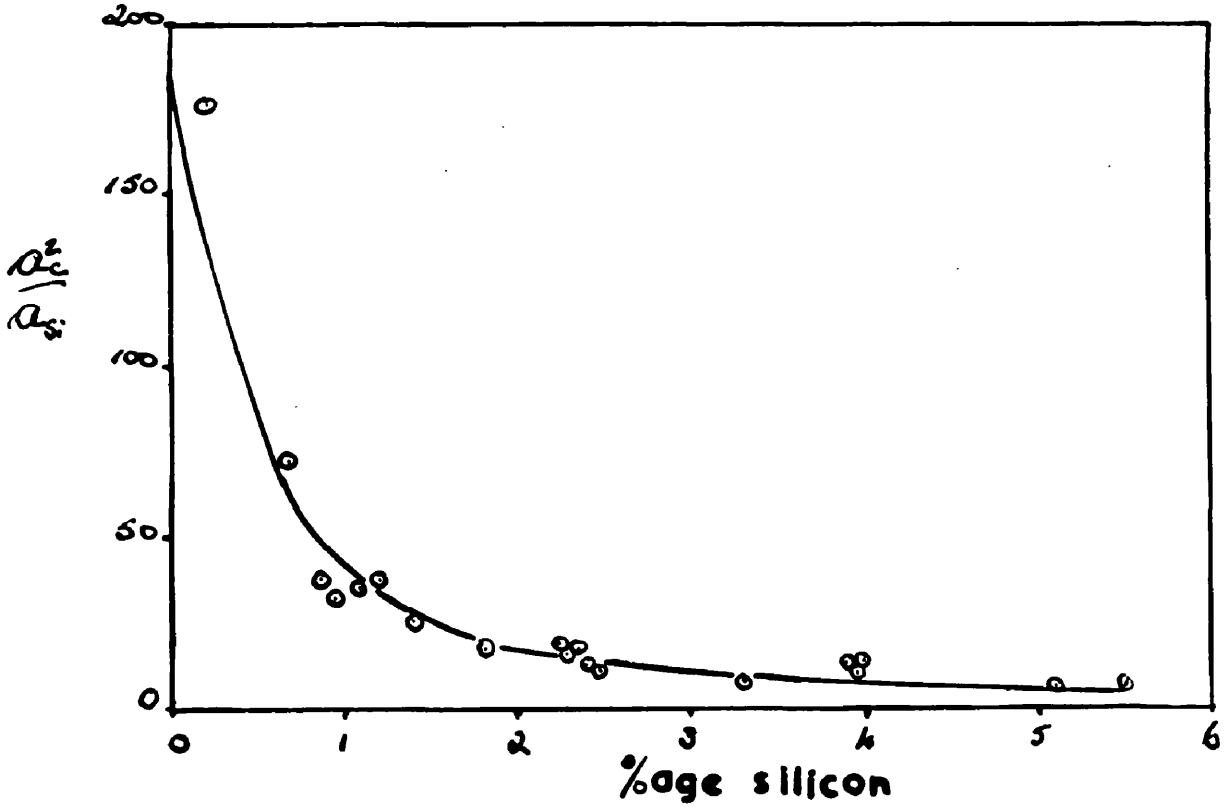
Values of $\frac{a_c^2}{a_{Si}}$ and $\frac{a_c^2}{a^*_{Si}}$ are shown in Table (16). As can be seen these ratios are not constant although they vary in a fairly regular manner with the percentage of silicon, Figs (21) and (22). Assuming that the estimated value of the activity of silica and the thermodynamic data used in calculating K_{Si} and K_c are correct then it is the ratios

Table (16)

Run A	$\frac{a^2_c}{a_{Si}}$	$\frac{a^2_c}{a^{**}_{Si}}$
11	176	192
12	72.5	94
13	38.8	53
14	33.3	47
15	35.8	51.6
16	38.4	58.5
17	25.3	39.6
18	17.4	29.8
19	19.3	35.8
20	15.6	29.0
21	16.7	31.4
22	12.6	23.8
23	11.4	27.2
24	7.8	16.8
25	12.9	29.8
26	13.0	30.0
27	13.0	29.8
28	5.4	13.4
29	5.65	14.4



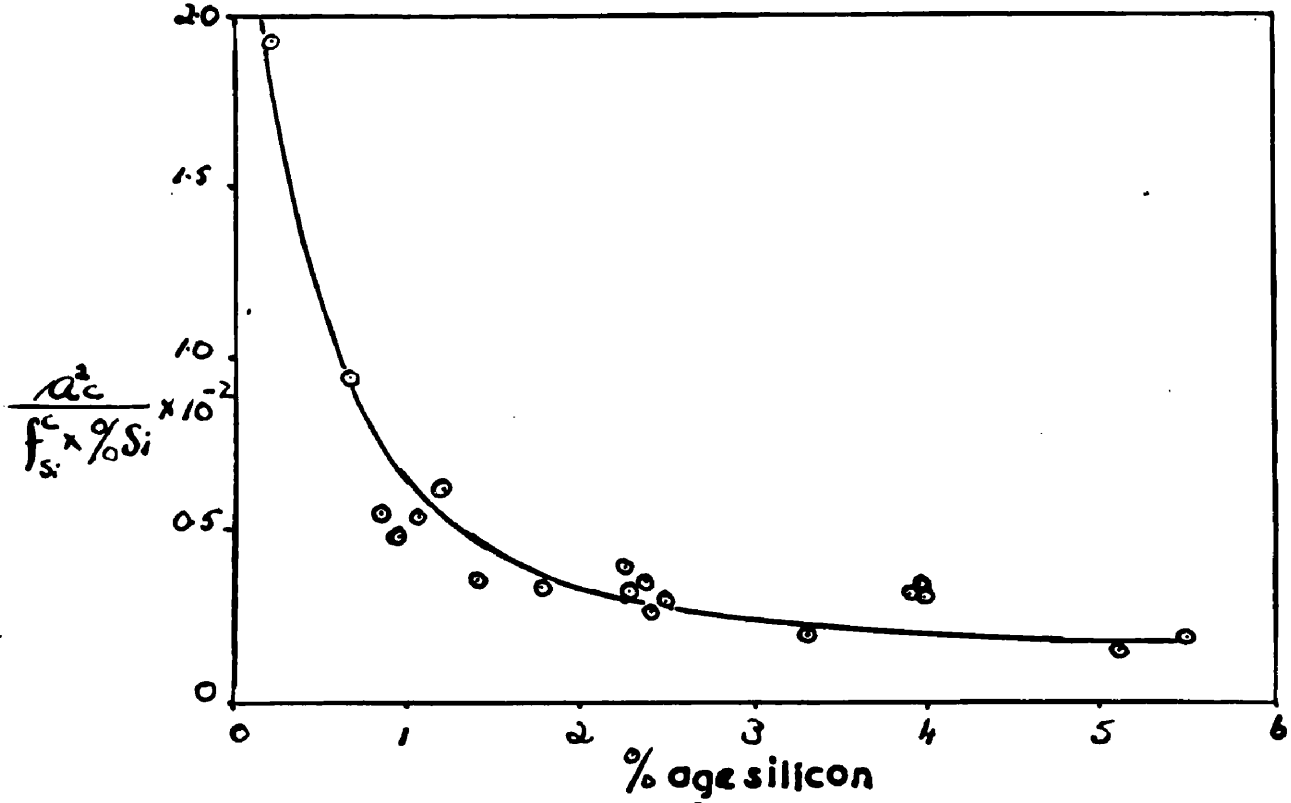
Fig(21) Variation of the ratio $\frac{a_c^2}{a_{Si}^2}$ with percentage silicon



Fig(22) Variation of the ratio $\frac{a_c^2}{a_{Si}^2}$ with percentage silicon

of $\frac{a^2_C}{a_{Si}}$ in the low silicon runs which are too high, i.e. the activities of carbon in these runs must be too high or the activities of silicon too low. From a consideration of the work on the activities of carbon and silicon presented in the previous chapter it would appear that it is most likely to be the activities of silicon which are in error. The experimental values of Marshall and Chipman[21] for the activity of carbon agree over a considerable range of composition with the theoretical values of Samarin and Shvartsman[23] and the experimental results on which the effect of silicon on the activity of carbon in iron-carbon-silicon ternary solutions is based is in good agreement with previously determined data[13]. On the other hand the two sets of values for the activity of silicon in iron silicon alloys differ considerably and the work on which the effect of carbon on the activity of silicon is based is open to criticism.

Moreover, if the variation in the ratio $\frac{a^2_C}{a_{Si}}$ were due entirely to errors in the activity of carbon then this would mean that the carbon activities corresponding to low silicons would have to be decreased by at least a factor of 3. As these activities are of the order of 12 this would mean reducing them to the highly improbable value of four. It would thus appear that the variation in the ratio $\frac{a^2_C}{a_{Si}}$ is largely, if not entirely, due to an incorrectly estimated activity of silicon.



Fig(23) Variation of $\frac{a_c^2}{f_{Si}^c \times \%Si}$ with percentage silicon

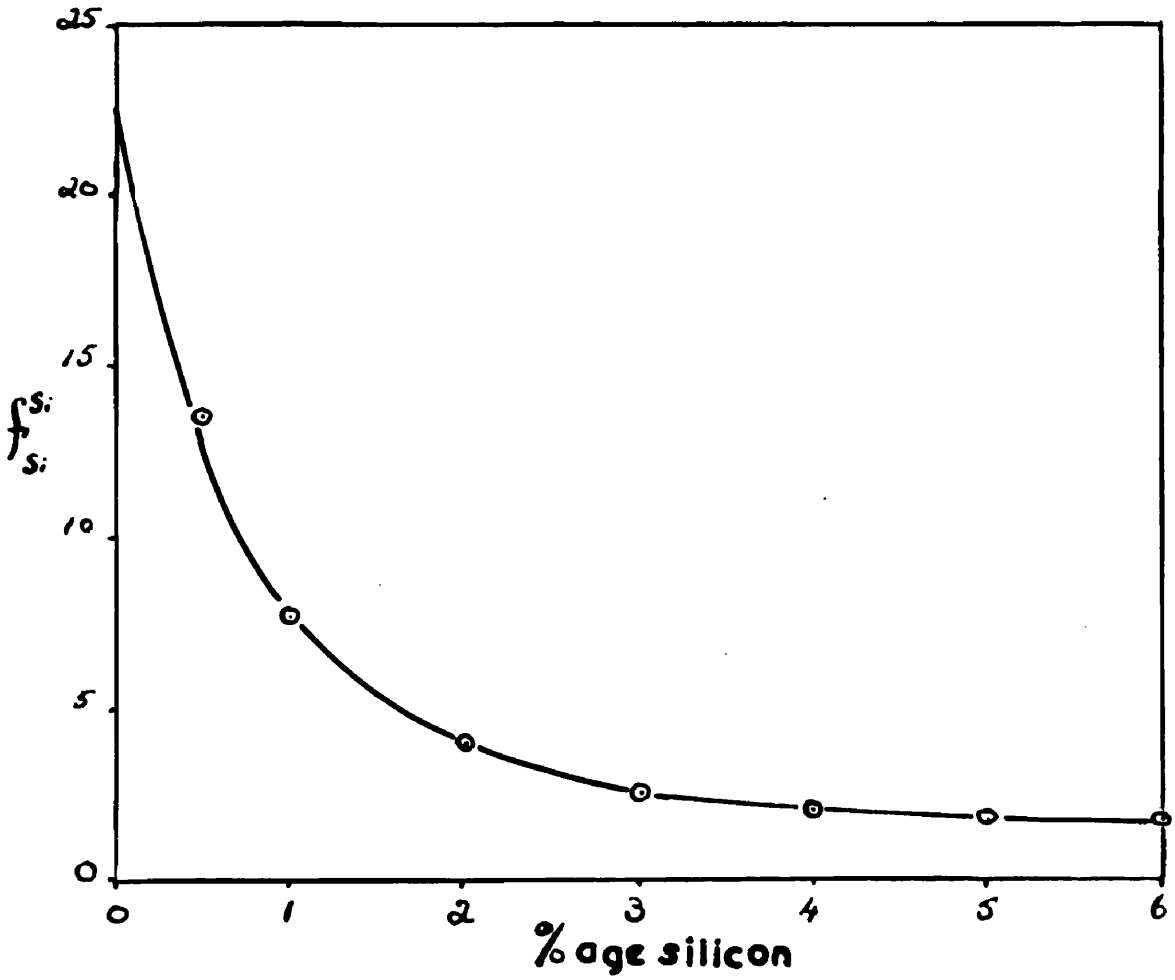


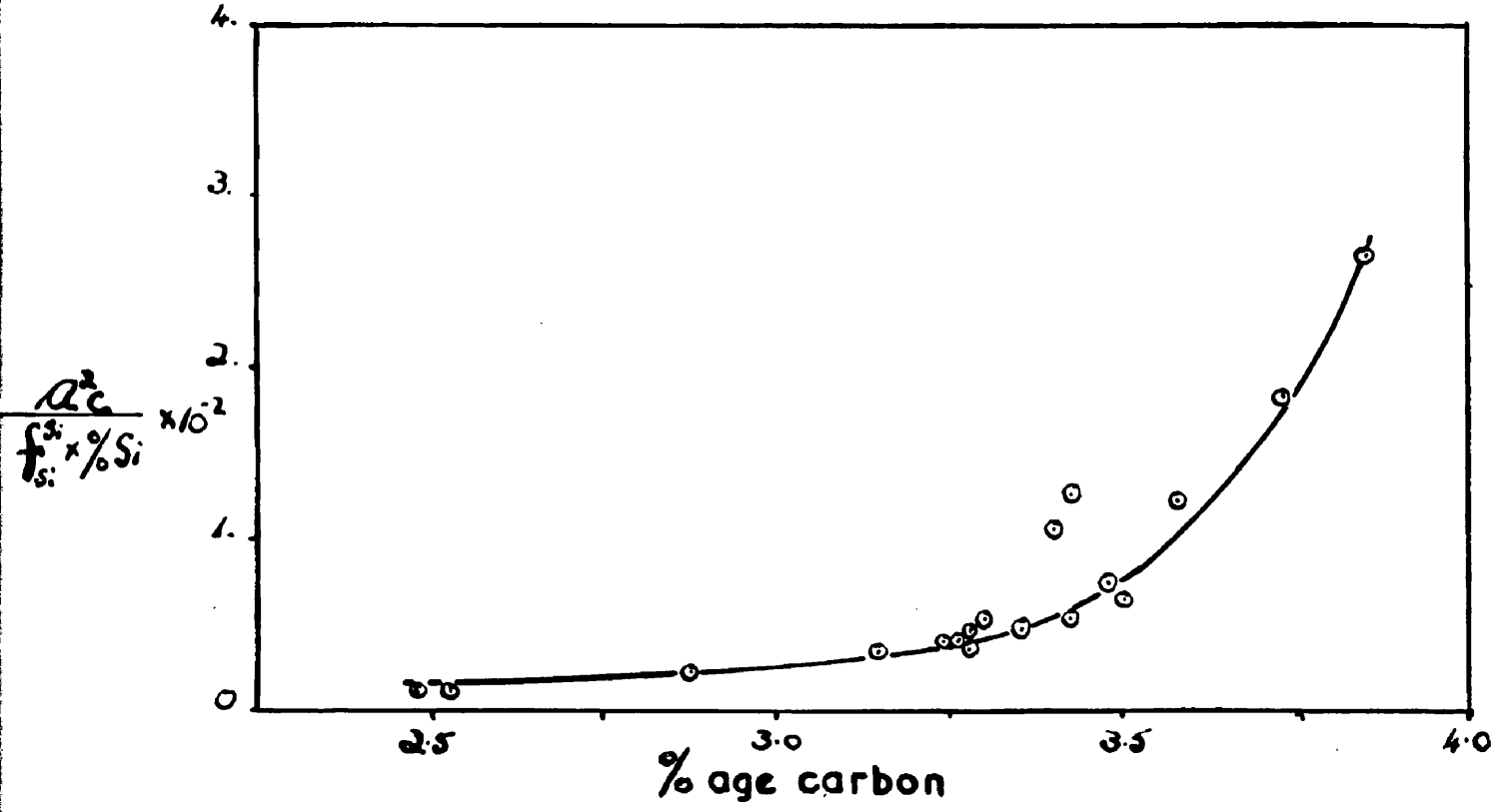
Fig.(24) Variation of the values of f_{Si}^{Si}, calculated from Fig (23), with percentage silicon

The activity of silicon in iron carbon silicon alloys is given by the expression

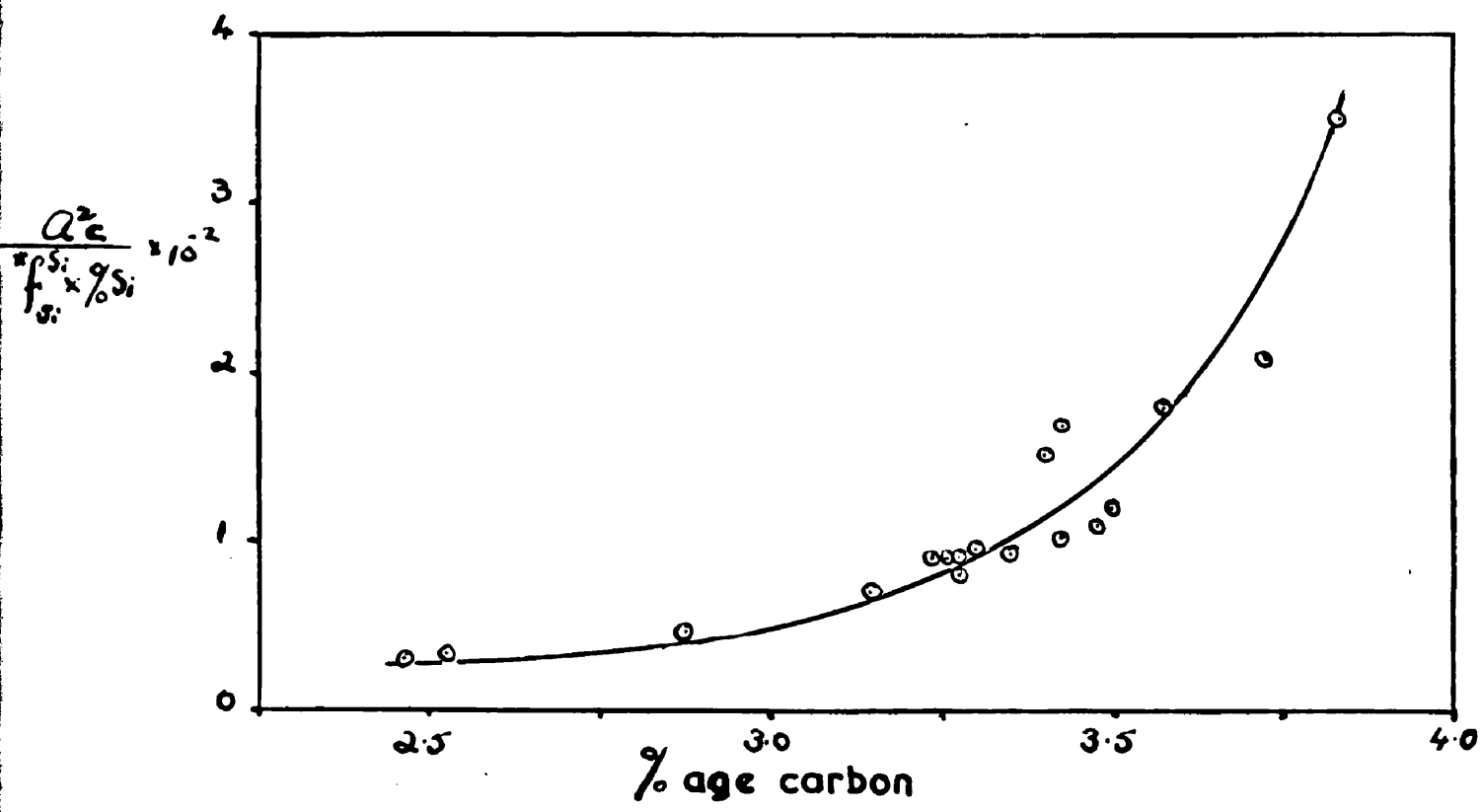
$a_{Si} = f^{Si}_{Si} \times f^{C}_{Si} \times \%Si$ where the activity coefficients are as defined in the previous chapter. An error in the assessment of the activity of silicon can thus be due to an error in either or both of these activity coefficients. In an attempt to determine whether the discrepancy would be attributed wholly to one or other of these coefficients it was assumed firstly that the values of f^{C}_{Si} given by Chipman (13) were correct and new values of f^{Si}_{Si} were calculated. The alternative case in which f^{Si}_{Si} was taken as correct and values of f^{C}_{Si} calculated was also examined.

In Fig. (23) is shown a plot of $\frac{a^2_c}{f^{C}_{Si} \times \% Si}$ against the percentage of silicon. Provided f^{C}_{Si} is correct any variation in this ratio can be attributed solely to a variation in f^{Si}_{Si}. The values of f^{Si}_{Si} required to make the ratio constant at 8.5 are shown plotted against the silicon content in Fig. (24). The large difference between these values of f^{Si}_{Si} and theoretical requirements (i.e. $f^{Si}_{Si} = 1$ at $\% Si = 0$) would suggest that it is the values of f^{C}_{Si} which are in error.

Considering the other, and more probable alternative, i.e. that the values of f^{Si}_{Si} as determined by Gokcen and Chipman (12) are correct and f^{C}_{Si} is in error, a ratio $\frac{a^2_c}{f^{Si}_{Si} \times \% Si}$ has been calculated. Any variation in this ratio should thus be due to a variation in f^{C}_{Si}. As f^{C}_{Si} is a



Fig(25) Variation of the ratio $\frac{\alpha^2_c}{f^{Si}_{Si} \times \%Si}$ with percentage carbon



Fig(26) Variation of the ratio $\frac{\alpha^2_c}{f^{Si}_{Si} \times \%Si}$ with percentage carbon

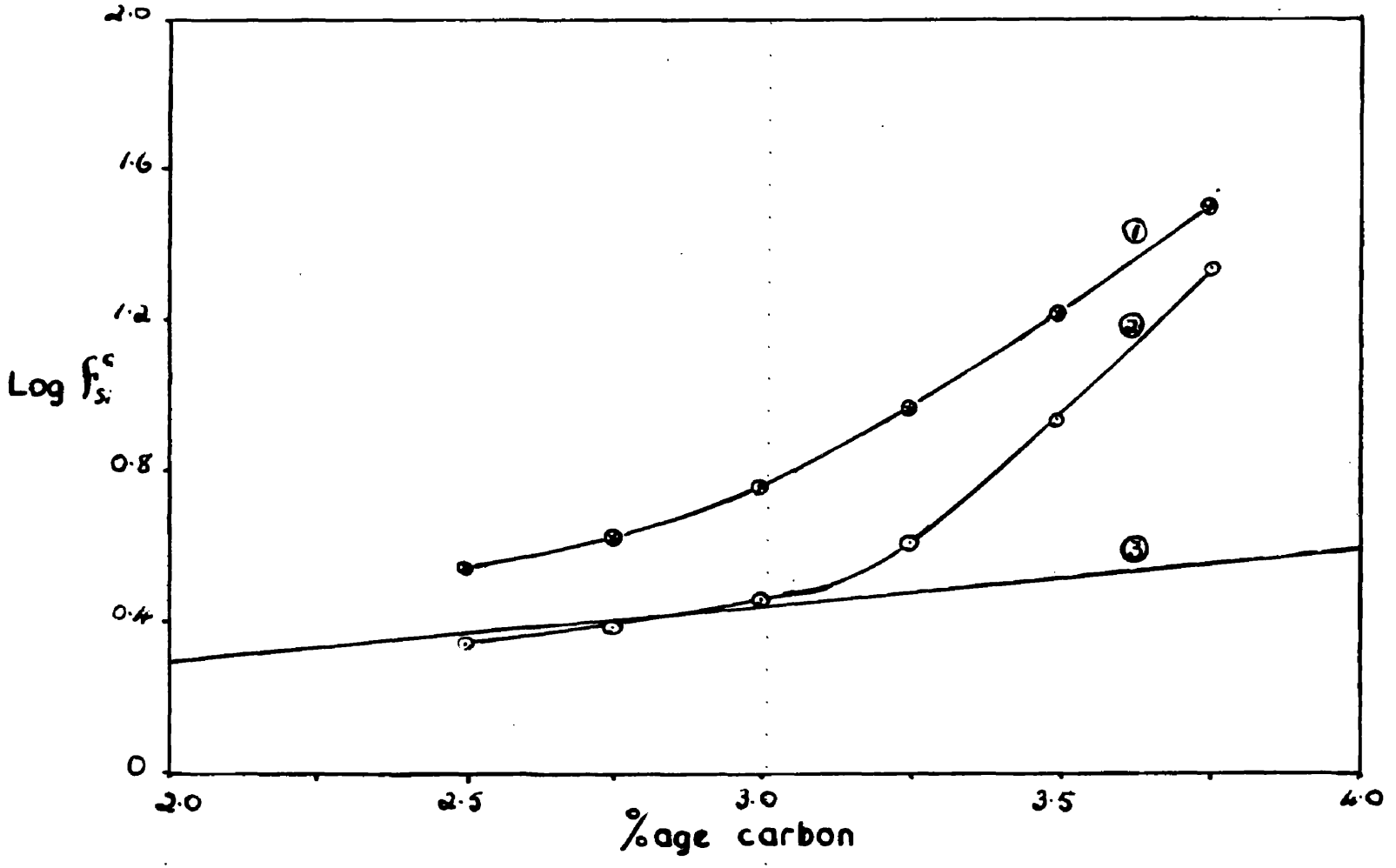


Fig. (27) Variation of Log f^{c}_{Si} with percentage carbon

① Values calculated from experimental results assuming $^{a}f^{Si}_{Si}$ correct

② " " " " " " f^{Si}_{Si} "

③ Chipman's[13] values

function of the carbon content, the ratio in this case has been plotted against the percentage carbon, Fig. (25). Again the ratio is not constant but varies in a fairly regular manner with the carbon content. Using the values of f_{Si}^{Si} obtained by Chipman[13] a similar relationship is obtained, Fig. (26). The values of f_{Si}^{C} required to make the ratios constant at 8.5 have been calculated in both cases and these are shown plotted against the carbon content in Fig. (27). Also shown are the values of f_{Si}^{C} calculated by Chipman[13] from Körbers[18] results. The values calculated in the present work using Gokcen's and Chipman's[12] values of f_{Si}^{Si} agree with Chipman's[13] results in the lower carbon ranges but diverge greatly above 3.0% carbon.

Using the second set of values of f_{Si}^{C} here calculated, the values of f_{Si}^{Si} as given by Gokcen and Chipman[12] and the values for the activity of FeO as obtained from the carbon results, new values of the product $\frac{a_{Si} \times a^2_{FeO}}{a^2_{Fe}}$, designated $^3K_{Si}$, have been calculated. These are shown in Table (17) and although there is still considerable variation, a reflection of the scatter of the points in Figs. (25) and (26) it is much less than was previously the case. ($'K_{Si}$). Using the first set of values of f_{Si}^{C} and Chipman's[13] values of f_{Si}^{Si}, $^3K_{Si}^{*}$ Has been calculated and which shows similar variations. Table (17).

Table (17)

A	$^3K_{Si} \times 10^6$	$^3K^{*}_{Si} \times 10^6$
11	4.01	6.55
12	19.9	22.6
13	9.2	13.0
14	9.5	13.6
15	22.0	25.6
16	23.4	24.6
17	28.0	32.5
18	24.8	30.5
19	41.5	41.0
20	26.8	29.2
21	39.5	40.2
22	19.8	22.6
23	24.2	27.9
24	20.5	17.6
25	31.8	31.4
26	28.5	27.4
27	27.0	26.0
28	15.6	9.3
29	17.4	9.3

(d) (i) The reaction $2C + SiO_2 = Si + 2CO$

In order to determine the silicon content of iron in equilibrium with a slag of the composition 41% Al_2O_3, 28% SiO_2, 31% CaO when the oxygen potential is controlled by the reaction,

$$2C + O_2 = 2CO$$

a series of experiments was done in carbon crucibles at 1500°C. The chemical analyses of samples taken from the metal and slag are shown in Table (18). The "initial metal" sample was taken immediately prior to, and the final sample taken 6 hours after, the addition of the preformed slag. The slag was made by fusing a mixture of the pure oxides CaO, Al_2O_3 and SiO_2. The final slag analyses show that the composition in each case approximates closely to that desired. By using the absorptiometric method described in Chapter (3) the small FeO content of the slags was also determined.

The variation of the silicon content with time in the various runs is shown in Fig. (28). In run A(36) in which no silicon was present initially the silicon rose from 0 to 1.1% after 6 hours at 1500°C, the major part of the reduction taking place in the first hour. In view of this slow rate of reduction a varying amount of silicon was added to the metal initially and in runs containing less than 20% Si this initial silicon content increased very slightly over the time of the experiment. In runs containing more than 20% Si there was a slight decrease. The silicon content in the run containing 20.7% silicon remained constant over the time of the experiment.

Table (18)

Run A	Metal			Slag				a_{Fe}	$\frac{\%FeO}{a_{Fe}}$
	Initial Si	Final Si	Final C	FeO	SiO_2	CaO	Al_2O_3		
36	0	1.1	4.80	0.11	28.0	31.5	40.5	0.58	0.19
37	4.45	4.79	3.75	0.08	28.6	30.7	41.0	0.50	0.16
38	6.80	6.99	3.20	0.04	28.8	30.7	-	0.45	0.09
39	8.56	8.80	2.60	0.05	27.8	31.3	40.5	0.41	0.12
40	13.2	13.4	1.75	0.02	28.5	30.5	41.2	ca.0.3	ca.0.07
41	16.9	17.1	1.25	0.02	27.9	31.2	41.3	-	-
42	20.7	20.7	0.80	0.02	28.3	31.5	-	-	-
43	25.4	24.8	0.60	0.02	28.0	30.6	-	-	-
44	27.2	27.0	0.57	0.02	27.5	30.9	40.6	-	-
45	0	0	5.15	0.02	0	50.0	50.0	0.59	0.03

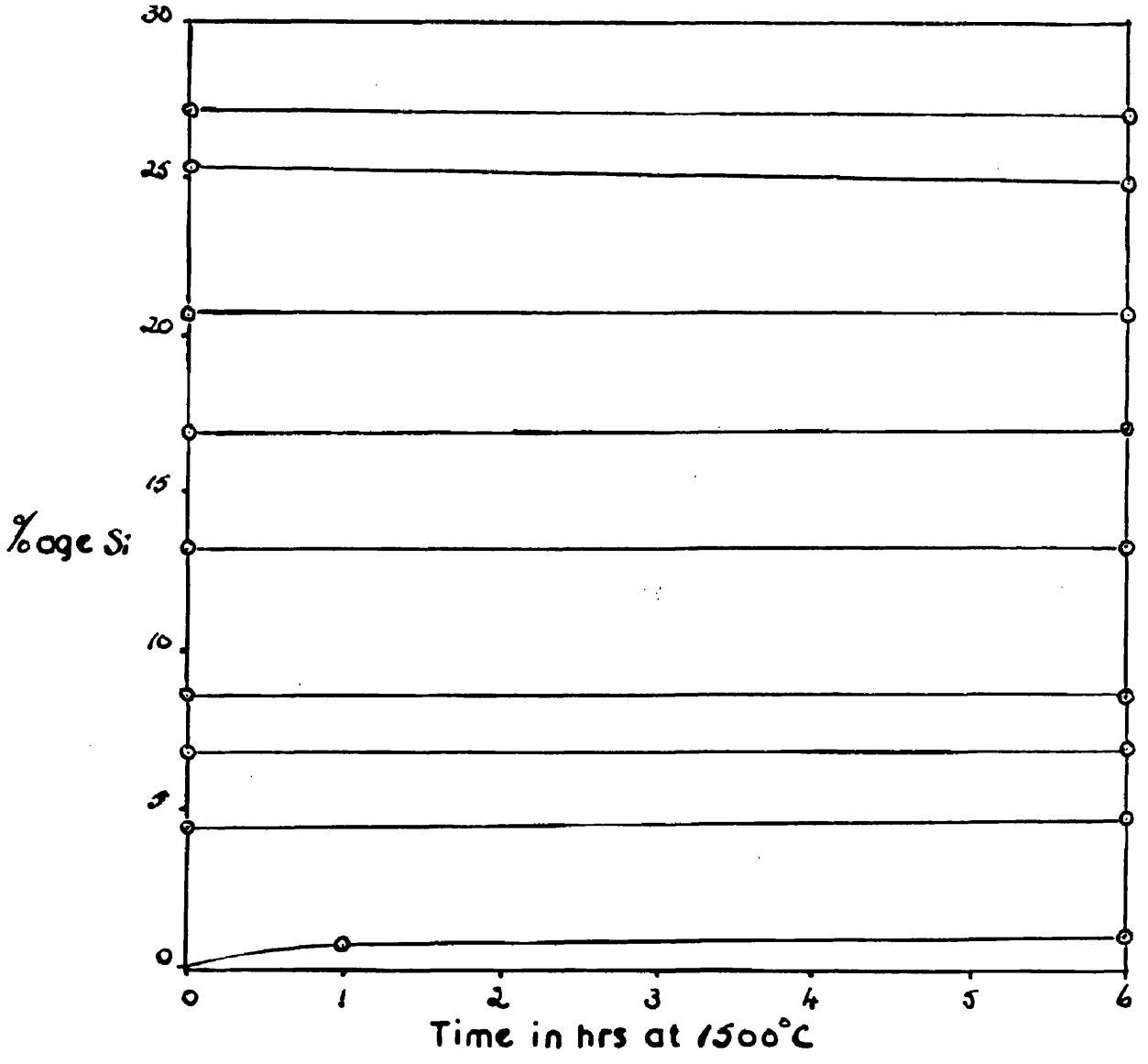


Fig. (28) Variation with time of the silicon content of carbon saturated iron under a 31% CaO, 41% Al_2O_3, 28% Si_2O slag.

As discussed in Chapter (3) the partial pressure of carbon monoxide can be taken as being equal to 1 atmosphere when bubbles of CO are being produced at the slag metal interface. However, when the silicon content of the metal is equal to, or above, the equilibrium value and CO is not being produced the partial pressure of CO in the reaction,

$$\underline{Si} + 2CO = (SiO_2) + 2C$$

must be taken as that in the atmosphere above the slag which in this case is of the order of $\frac{1}{3}$ atmosphere. Other variables being equal, the above reaction would only proceed under a CO pressure of one third of an atmosphere when the silicon content of the metal was such that the activity of silicon was 9 times $\left\{ \frac{1}{\frac{1}{(3)}^2} \right\}$ the equilibrium value under a CO pressure of 1 atmosphere. From the present results this equilibrium value lies somewhere between 17.2 and 20.7% Si so that it would appear unlikely that the activity of silicon in metal containing 25 and 27% Si is 9 times the equilibrium value. For this reason it is thought that the decrease in the silicon content in Runs A43 and 44 is due to some other mechanism than oxidation by carbon monoxide.

(ii) <u>The Formation of Silicon Carbide</u>

During Run A44, it was observed that when the metal containing approximately 27% silicon was melted in a graphite crucible at 1500°C a brown powdery substance remained floating on the surface of the metal. This substance was skimmed off and identified by means of x-rays as the cubic or β modification of silicon carbide. The diffraction

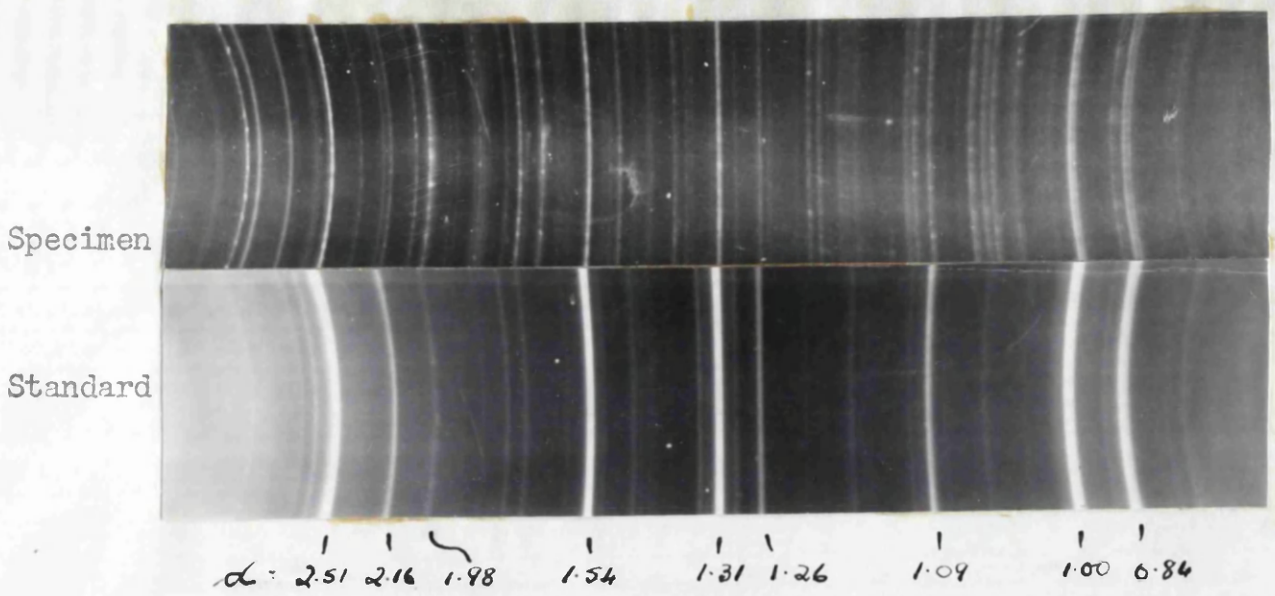
photograph is shown in Fig. (29) along with a photograph of silicon carbide prepared by heating a mixture of silicon and graphite in a graphite crucible at 1500°C. The silicon carbide prepared in this way had a light green colour. The strong cubic pattern on both pictures match well and show excellent agreement with the published data on β silicon carbide as given in the A.S.T.M. index. Although silicon carbide was not identified in Run A43 it would be reasonable to suppose that the reduction in the silicon content in the metal during experiments A44 and 43 was due to the slow separation of silicon carbide formed by the reaction

$$Si_{(in\ Fe)} + C = SiC$$

Thus, it can be said, that under a CO pressure of 1 atmosphere the silicon content of metal in equilibrium at 1500°C with a slag of the composition 31% CaO, 28% SiO_2, 41% Al_2O_3 lies between 17.2 and 20.7% and that metal in equilibrium at 1500°C with both solid graphite and silicon carbide contains between 20.7 and 25.0% silicon. Unfortunately, time did not permit the fixing of these equilibria within closer limits and it has been assumed in each case that the equilibrium positions lie at the mean of the two ranges i.e. at 19% Si and 23.0% Si respectively.

(iii) <u>The activity of silicon in iron containing 23% Si, 0.70%C</u>

The fact that metal of this composition is in equilibrium with silicon carbide allows a value of the activity of silicon to be



d $\overset{o}{A}$	I/I_o
2.51	100
2.17	20
1.54	63
1.31	50
1.26	5
1.09	6
1.00	18
0.84	10

A.S.T.M. standard for β SiC.

Fig. (29)

calculated which is independent of the activity coefficients previously determined[12], [13]. Thus the free energy change accompanying the reaction

$$Si_{(liq)} + C = SiC$$

is equal to $- RT \log_e K$ where $K = \frac{a_{SiC}}{a_{Si} \times a_C}$. As both carbon and silicon carbide are present in the solid state their activities can be taken as unity and the activity of silicon determined.

Several expressions for the free energy of formation of silicon carbide from liquid silicon and solid carbon are quoted in the literature. Some of these are shown in Table (19) along with the source from which they have been derived.

Table (19)

ΔG^o	Quoted by	Source
$-37,800 + 8.6\ T$	Quill[31]	(Kelley[34] (Chipman and Grant[35]
$-37,200 + 7.4\ T$	Kubaschewski[32]	(Weibke and Kubaschewski[36] (Bichowsky and Rossini[37] (Kelley[34] [38].
$-38,400 + 8.5\ T$	Chipman[17]	No reference
$-26,500 + 12.1\ T$	Remin[31]	Schenk[39]

Using the expression quoted by Quill[31] a value of ΔG^o at 1500°C of -22,500 cals is obtained and therefrom an activity of silicon

of 1.7×10^{-3} on the pure scale. On the dilute solution scale this activity is equal to $3.3 \left(\frac{1.7 \times 10^{-3}}{0.00047}\right)$. Similar values (2 and 3 respectively) are obtained using the second and third expressions.

Although an accurate value of the activity of silicon in metal of this composition (23% Si, 0.70%C) can not be obtained from the published values of the activity coefficients of silicon, an approximate value can be estimated. At 15% Si the value of f_{Si}^{Si} given by Gokcen and Chipman[12] is 3.77 and by a rather lengthy extrapolation from 15 to 23% silicon an approximate value of 4.0 is obtained for 23% silicon. The value of f_{Si}^{C} given by Chipman[13] for the carbon content is 1.3. The activity of silicon is therefore approximately 120 and there is thus a large discrepancy between the values of the activity of silicon calculated by these two methods.

Using the free energy expression quoted by Remin[33] a value for the activity of silicon of 7,000 on the dilute solution scale is obtained so that an equally large discrepancy exists in this case.

Recently a new value has been obtained [40] for the heat of combustion of β silicon carbide and from this an expression for the free energy of formation of β SiC from liquid silicon and solid graphite has been derived[41].

This expression,

$$\Delta G^{\circ} = -24,010 + 8.33T.$$

gives at 1500°C a value of ΔG° of - 9,240 cals. from which has been

obtained a value of the activity of silicon of 0.076 on the pure scale or of 161 on the dilute solution scale. This value is of the same order as that calculated using the available activity coefficients and for this reason it is considered that the above free energy expression for the formation of silicon carbide is more accurate than those previously published.

(iv) The activity coefficients of silicon

(i) f_{Si}^{Si}. In Fig. (30) are shown plots against the percentage silicon of the activities of silicon in iron-silicon alloys obtained by Gokcen and Chipman[12] and by Chipman[13]. Above 4% silicon the activities found by Gokcen and Chipman increase linearly with silicon content. Also marked in the figure is the activity of silicon in the alloy 23% Si, 0.7% C (⊙) obtained from the thermodynamic data on silicon carbide. This activity is higher than that in the plain 23% Si alloy by the factor f_{Si}^{C} corresponding to 0.7% carbon. Taking the value given by Chipman[13] of 1.3 which is probably approximately correct at this low carbon percentage then the corresponding activity in the binary alloy is 125, marked ⊗. This value is much higher than the activity calculated by Chipman[13] for this alloy and does not lie on the extrapolated straight line of Gokcen and Chipman[12]. In fact a large deviation from linearity would have to occur between 15 and 23% silicon before the two results could be reconciled.

Examination of the results of Gokcen and Chipman[12] reveals that above 2% silicon the activity coefficients are based on only three experimental points. For these reasons it is considered

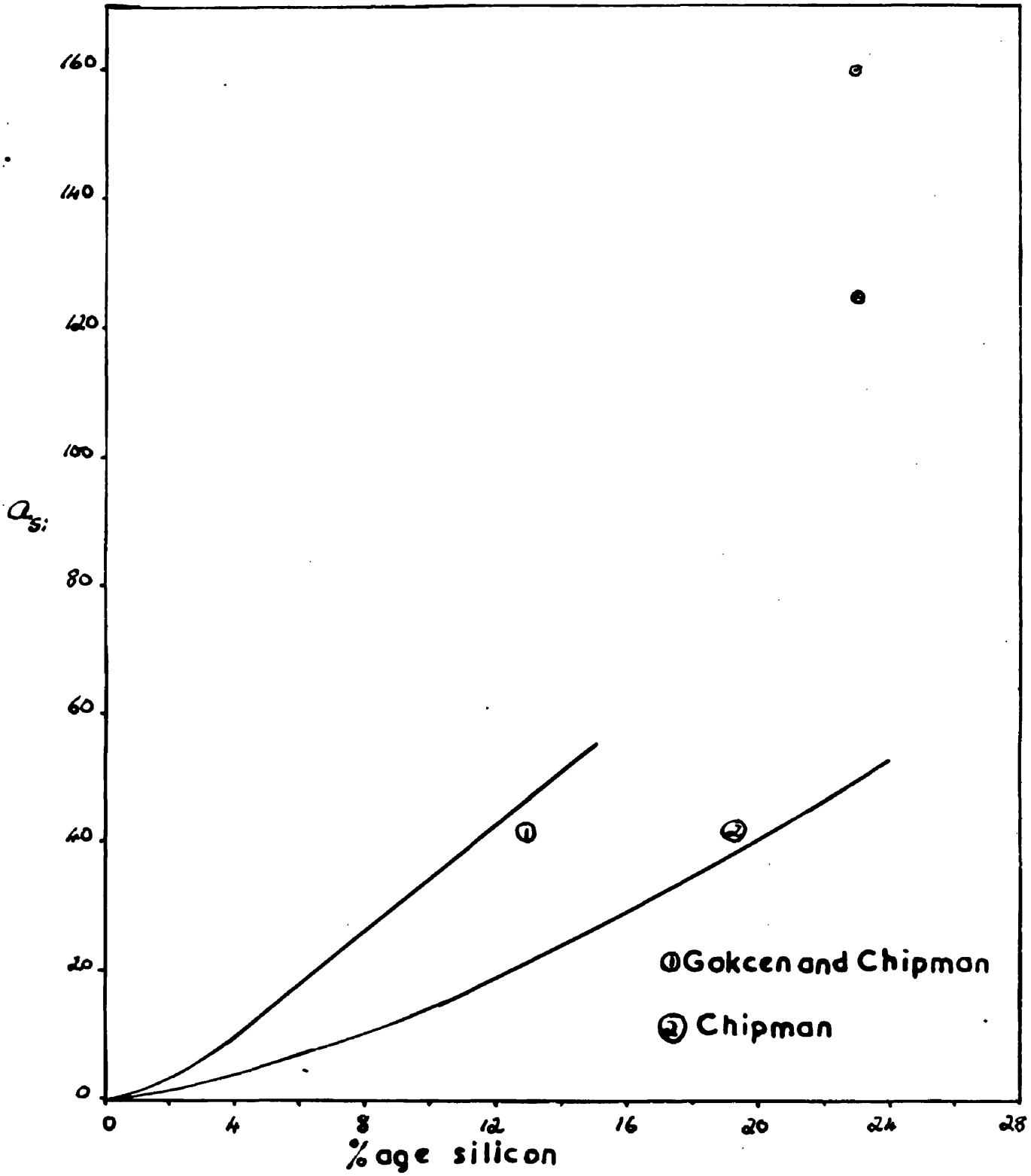


Fig.(30) Comparison between the activities of silicon in iron of Chipman[13] and of Gokcen and Chipman[12] with the value calculated from the free energy of formation of silicon carbide

that both the values of f_{Si}^{Si} of Gokcen and Chipman[12] and of Chipman[13] are too low in at least the higher silicon ranges.

(ii) f_{Si}^{C}. The existing values of f_{Si}^{C}, the effect of carbon on the activity coefficient of silicon, put forward by Chipman[13] have been criticised in the previous chapter. In the present work two sets of values have been calculated; one assuming that the values of f_{Si}^{Si} of Chipman[13] are correct and the other that those of Gokcen and Chipman[12] are correct. From the above discussion it is evident that neither of these assumptions are correct although the latter is probably approximately so when the range 0~5% silicon only is considered. Therefore, of the two sets of values of f_{Si}^{C} herein calculated the second set are considered the more accurate. The correct values of f_{Si}^{Si} are probably slightly higher in the range 0~5% Si than those of Gokcen and Chipman[12] and this would result in slightly lower values of f_{Si}^{C}.

In the range 3-4% carbon the values of f_{Si}^{C} rise rapidly with increasing carbon content and therefore for the same silicon content a small increase in the percentage carbon in this range results in a large increase in the activity of silicon. It can be shown (p.82) that for a constant activity of silica in the slag an increase in temperature of from 1500°C to 1600°C should result in an eightfold increase in the activity of silicon in the underlying metal. In blast furnace practice it would therefore be expected that an increase in temperature, other factors remaining constant, would result in a large increase in the percentage silicon. This, however, is not the

case; temperature variations of up to 50°C causing only relatively small changes in the silicon content. As the temperature rises, however, so does the solubility of carbon and, as f_{Si}^{C} increases steeply with increasing carbon content, a higher activity of silicon results.

This picture is, of course, a simplification in-so-far as it has been assumed that equilibrium is attained in the blast furnace. There is little doubt that this is not the case[42] although it is probable that the system is displaced an approximately equivalent amount from equilibrium at each temperature.

Another simplification is that the presence of sulphur, phosphorus and manganese has been ignored. Before a complete analysis of the system could be attempted the effect of these elements on the activity of silicon would have to be known, i.e. f_{Si}^{S}, f_{Si}^{P} and f_{Si}^{Mn}, and also the effect at various temperatures of these elements on the solubility of carbon which in turn affects f_{Si}^{C}.

(v) <u>The activity of silica in the 31% CaO; 28% SiO_2; 41% Al_2O_3 slag</u>

Using the free energy expressions for the formation of CO and SiO_2 as given by Richardson and Jeffes[5] the equilibrium constant for the reaction

$$SiO_2 + 2C = Si + 2CO$$

can be calculated.

Thus;

$2C + O_2 = 2CO$	$\Delta G^\circ = -53,400 - 41.90T$
$Si + O_2 = SiO_2$	$\Delta G^\circ = -217,600 + 48.79T.$
$SiO_2 + 2C = Si + 2CO$	$\Delta G^\circ \quad 164,200 - 90.69T.$

At 1500°C

$$\Delta G^\circ = + 3,400 \text{ cals.}$$

whence $K = 0.38$ where $K = \dfrac{a_{Si} \times p^2_{CO}}{a_{SiO_2} \times a^2_C}$

Therefore when $p_{CO} = a_C = 1$

$$a_{SiO_2} = \frac{a_{Si}}{0.38.}$$

Although the activity of silicon in metal containing 19% Si and 0.90%C, the approximate composition of metal in equilibrium with the slag at 1500°C, cannot be obtained exactly a fairly close estimate can be made.

The activity of silicon in the 23.0% Si alloy has been found to be 161 from the silicon carbide data and, assuming that f_{Si} does not change in the range 19-23.0% Si, the activity in the 19% Si alloy will be $161 \times \frac{19}{23.0} = 133.$ f_{Si} is equal to $f^{Si}_{Si} \times f^{C}_{Si}$ and there is little doubt that f^{Si}_{Si} will decrease as the silicon content falls from 23.0 to 19%. On the other hand f^{C}_{Si} will increase because of the increased carbon content corresponding to the lower silicon

percentage. (Fig.10). Both changes should be small and as they are in opposite directions the overall change in f_{Si} should be negligible.

The activity of silica in the slag in equilibrium with the metal containing 19% silicon is thus

$$a_{SiO_2} = \frac{133 \times 0.00047}{0.38} \quad \text{or } 0.16.$$

Fulton, Grant and Chipman[3] in their study of the reaction

$$(SiO_2) + 2C = \underline{Si} + 2CO$$

at 1600°C also found that silicon carbide separated from carbon saturated iron containing 23% silicon. At 1600°C the free energy of formation of SiC from liquid silicon and graphite is -8,400 cals giving an activity of silicon in equilibrium with graphite and silicon carbide of 0.11 on the pure scale or of $\frac{0.11}{0.0007} = 157$ on the dilute solution scale. As it would be expected that f_{Si} is largely independent of temperature, the agreement between these two figures (161 and 157) to a large extent confirms the composition of the metal estimated in the present work to be in equilibrium with carbon and silicon carbide at 1500°C

At 1600°C the free energy change for the reaction

$$SiO_2 + 2C = Si + 2CO$$

is -5,600 cals, giving a value of $K = \frac{a_{Si} \times p^2_{CO}}{a_{SiO_2} \times a^2_C}$ of 4.50. The work of Fulton, Grant and Chipman was done in carbon crucibles under

a CO pressure of 1 atmosphere so that the constant reduces to $K = \frac{a_{Si}}{a_{SiO_2}}$. The activity of silica in the slags in equilibrium with the metals containing 2% silicon is thus $\frac{0.11}{4.50}$ or 0.025. This value is approximately 7 times smaller than that calculated from the diagram of Rey, Figs (15) and (16), but from a consideration of the thermodynamic data it can be shown that it is most probably the latter values that are in error.

This can best be done by calculating the ratio of the activities of silica at 1500°C and 1600°C which give the same equilibrium percentage of silicon in the metal at these two temperatures.

Thus,

$a_{Si} = f_{Si}$ x %Si on dilute solution scale.

$= f_{Si}$ x %Si x 0.0007 on pure scale at 1600°C.

or $= f_{Si}$ x %Si x 0.00047 on pure scale at 1500°C.

The activity of silica in the slag in equilibrium with this activity of silicon at 1600°C is

$$a_{SiO_2}^{1600^\circ C} = \frac{f_{Si} \times \%Si \times 0.0007}{4.50}$$

and at 1500°C

$$a_{SiO_2}^{1500^\circ C} = \frac{f_{Si} \times \%Si \times 0.00047}{0.38}$$

so that

$$\frac{a_{SiO_2}^{1500^\circ C}}{a_{SiO_2}^{1600^\circ C}} = \frac{f_{Si} \times \%Si \times 0.00047}{0.38} \times \frac{4.50}{f_{Si} \times \%Si \times 0.0007}$$

Making the reasonable assumption that f_{Si} is the same at 1600°C as it is at 1500°C, then

$$\frac{a_{SiO_2}^{1500^\circ C}}{a_{SiO_2}^{1600^\circ C}} = 8$$

i.e. in order to obtain the same percentages of silicon in the metal at 1500°C as Fulton, Grant and Chipman obtained at 1600°C. the appropriate silica activities must be multiplied by 8. (Conversely for equal silica activities an increase in temperature of from 1500°C to 1600°C results in an eightfold increase in the activity of silicon). Taking the values of Rey (Fig. 16) and remembering that the activity of silica cannot be greater than unity it is only possible to multiply by 8 where the equilibrium silicon content of the metal is less than 20%, i.e. at 1500°C, 20% would be the silicon content of metal in equilibrium with a slag saturated with silica. In the present work, however, it has been found that at 1500°C the silicon content of metal in equilibrium with a slag far removed from silica saturation is 19% so that, assuming the thermodynamic data on the reduction of silica by carbon is correct, the values for the activity of silica given by Rey[28] in the range considered are too high.

(vi) The FeO content of the slags .

An important feature of the results of the runs done in carbon crucibles is the FeO content of the slags. The values are shown in Table (18) and are plotted against the silicon content in Fig. (31). The FeO figures are considered to be accurate within ± 0.01%. As can be seen from Fig. (31) the FeO content falls from 0.11% at 1.1%Si to

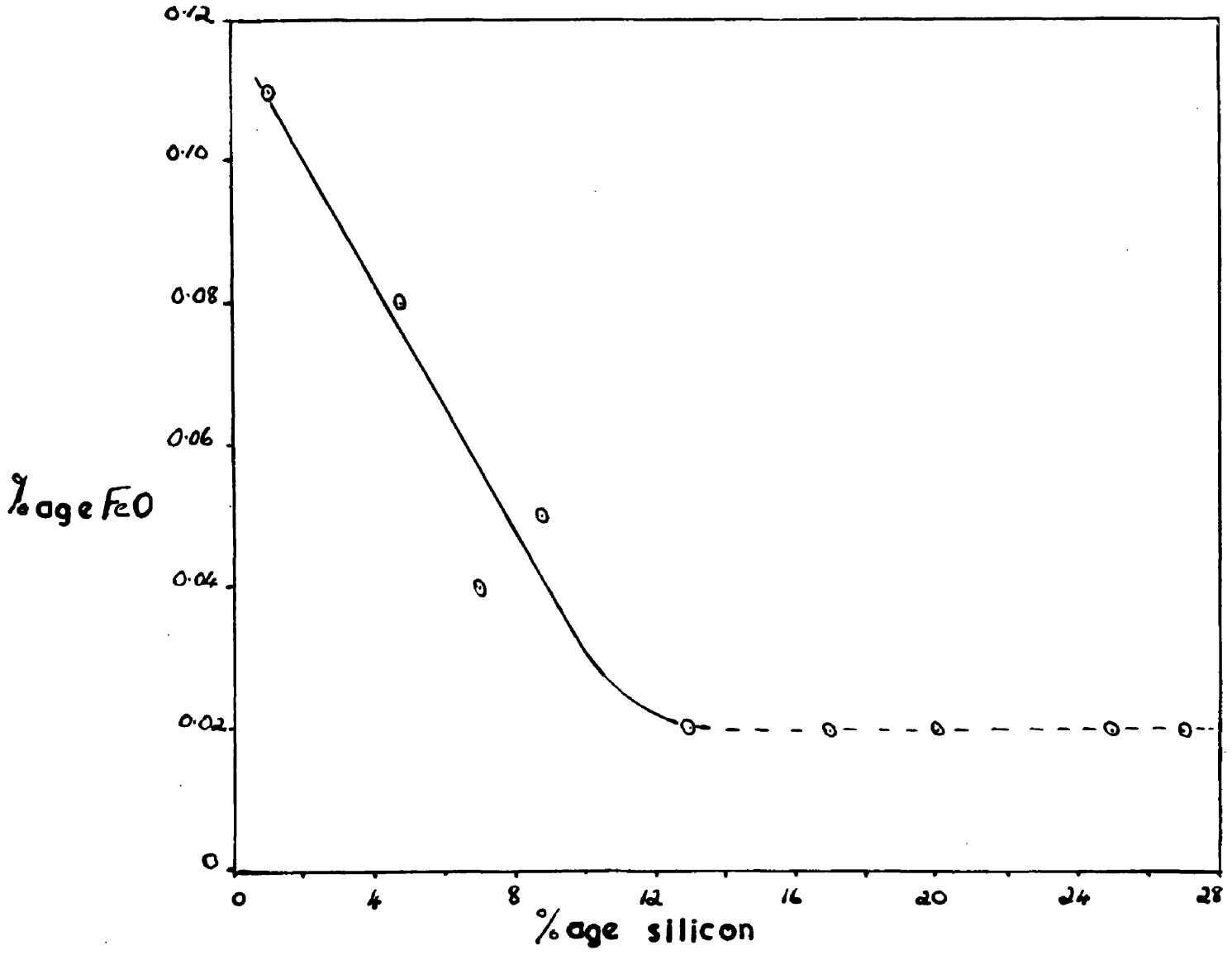


Fig. (31) Variation of FeO content of slag with silicon content of metal (carbon crucible experiments)

0.02% at 13% silicon. Beyond 13% silicon the method of analysis is insufficiently accurate to determine whether there is a continuing decrease.

The presence of FeO in the slags would suggest that the reduction of silica by carbon takes place in two stages,

$$\text{(i)} \quad (SiO_2) + 2Fe = \underline{Si} + 2\,(FeO)$$

$$\text{(ii)} \quad 2\,(FeO) + 2C = 2\,\underline{Fe} + 2CO$$

$$\text{(iii)} \quad (SiO_2) + 2C = \underline{Si} + 2CO$$

If the second reaction comes to equilibrium then $K = \frac{a^2_{\underline{Fe}} \times p^2_{CO}}{a^2_C \times a^2_{FeO}}$ so that when $a_C = p_{CO} = 1$ the ratio of the activity of iron to the activity of FeO should be constant and assuming that in the small range 0.02 to 0.11% the percentage of FeO is proportional to the activity then the ratio $\frac{\%\underline{FeO}}{a_{\underline{Fe}}}$ should also be constant. By the method described in the previous chapter the activity of iron has been calculated up to 8.8% silicon and the ratio $\frac{\%\underline{FeO}}{a_{\underline{Fe}}}$ calculated. To extend the method to the subsequent runs would involve a large extrapolation of the curve of log f_C against carbon content, Fig.(12), which is hardly justified. However it would appear unlikely that the activity of iron in Run A(40) would be less than 0.3 giving a ratio $\frac{\%\underline{FeO}}{a_{\underline{Fe}}}$ of 0.07 and taking this result together with the preceding ones there is little doubt that the ratio is decreasing.

It would thus appear that reaction (ii) does not come to equilibrium but that at low silicon contents a higher than equilibrium content of FeO is present in the slags. In other words when reaction (i) is far from equilibrium it proceeds at a faster rate than reaction (ii).

In run A(45) a plain lime-alumina slag was melted in a graphite crucible, FeO added, and the temperature maintained at 1500°C for 3 hours. On analysis this slag was found to contain 0.02% FeO and as there was no silicon present in the metal the ratio $\frac{\%FeO}{a_{Fe}} = \frac{0.02}{0.59} = 0.03$. Thus when there is no silica present and FeO is not being continually produced in small quantities by reaction (i), reaction (ii) approaches equilibrium much faster than when silica is present in the slag. Making the assumption that, at this low percentage the activity coefficient of FeO in the $CaO-Al_2O_3$ slag is not widely different from what it is in the $CaO-Al_2O_3-SiO_2$ slag, and taking 0.03 as being the equilibrium value of the ratio $\frac{\%FeO}{a_{Fe}}$ then the equilibrium FeO contents in runs A(36) to A(39) inclusive lie between 0.01 and 0.02.

The slowness of the reaction

$$C + (FeO) = \underline{Fe} + CO$$

at low FeO contents can not however explain the slow rate at which the reaction

$$\text{(iii)} \quad (SiO_2) + 2C = \underline{Si} + 2CO$$

proceeds. The highest FeO content observed in the experiments was 0.11% and as the equilibrium silicon content corresponding to this figure is at least 5% then it would be expected, if the reaction

$$(i) \quad (SiO_2) + 2Fe = \underline{Si} + 2(FeO)$$

were rapid, that the silicon content would rise to this figure before the reaction

$$(ii) \quad (FeO) + C = \underline{Fe} + CO$$

became the controlling reaction. It must therefore be assumed that reaction (i) is itself slow but that when far from equilibrium it proceeds at a rate greater than reaction (ii) proceeds at low FeO contents, i.e. FeO contents below 0.1%

The effect of silica reduction on the metal-slag transfer of sulphur

The most widely accepted view is that sulphur transfer takes place according to the reactions,

$$(iv) \quad \underline{FeS} = (FeS)$$

$$(v) \quad (FeS) + (CaO) = (FeO) + (CaS)$$

$$(vi) \quad \underline{FeS} + CaO = (FeO) + (CaS)$$

Rocca, Grant and Chipman[1] studied reaction (vi) in cases where the slag contained medium quantities of FeO i.e. 0.1% to 5%. They found that equilibrium was fairly rapidly attained and also that at low FeO contents a small increase in the FeO content of the slag resulted in a

large increase in the sulphur content of the metal.

In experiments carried out in carbon crucibles the FeO is reduced to a low figure according to the reaction.

$$(ii) \quad (FeO) + C = \underline{Fe} + CO$$

so that the overall reaction for the transfer of sulphur is

$$(vii) \quad \underline{FeS} + (CaO) + C = \underline{Fe} + (CaS) + CO.$$

This reaction has been found by Hatch and Chipman[2] and by Grant, Troili and Chipman[8] to proceed very slowly when the sulphur content of the metal is low, i.e. below about 0.1%. At higher sulphur contents the reaction proceeded rapidly. Grant, Troili and Chipman[8] also found that when a plain lime-alumina slag free of silica was used the reaction came quickly to equilibrium.

In view of the known slowness of reaction (ii) at low FeO contents this latter finding is at first sight, surprising. However reaction (ii) is likely to be the limiting reaction only at FeO contents below about 0.1% and at this stage the amount of sulphur still to be transferred to the slag is relatively small. For a slag of the composition used in the present work the difference in the equilibrium sulphur content of the metal produced by the presence of 0.1% FeO in the slag is of the order of 0.1%[4]. In a system containing equal slag and metal weights the transfer of this amount of sulphur corresponds to the production of approximately 0.2% FeO in the slag. Unless reaction (ii) is extremely slow this small

amount of FeO will be quickly reduced and the overall reaction

$$\text{(vii)} \quad \underline{FeS} + (CaO) + C = \underline{Fe} + (CaS) + CO$$

can come to equilibrium.

The picture changes, however, when the reduction of silica and the transfer of sulphur are taking place concurrently. When no silicon is present in the metal initially considerable reduction takes place from slag to metal. Fig. (32) which is reproduced from the paper of Grant, Troili and Chipman[8] shows that, from the slag used in their experiments, 1.75% silicon is reduced in 8 hours. In the present work the amount reduced in 6 hours was 1.1%. If the reaction

$$\text{(i)} \quad (SiO_2) + 2\underline{Fe} = \underline{Si} + 2(FeO)$$

is assumed to be operative, and equal slag and metal weights are present then the transfer of 1% silicon corresponds to the production of approximately 5% FeO in the slag. Unlike the FeO produced by the reaction

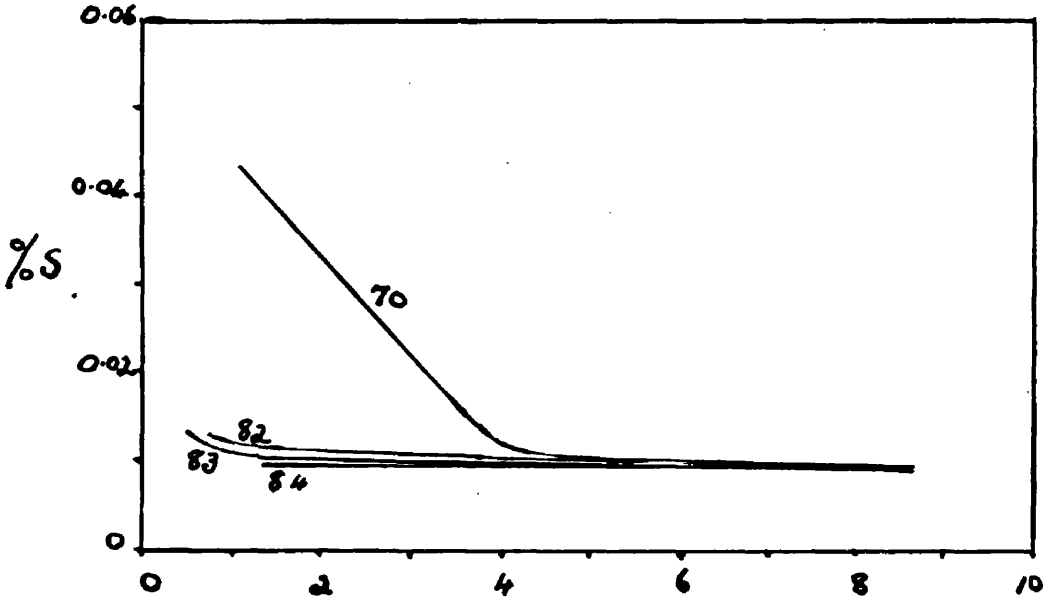
$$\text{(vi)} \quad \underline{FeS} + (CaO) = (CaS) + (FeO)$$

this FeO is being produced slowly so that the slag is at an oxygen potential higher than that corresponding to the equilibrium position of the reaction

$$\text{(ii)} \quad (FeO) + C = \underline{Fe} + CO$$

for a considerable period of time. The reaction

$$\text{(vii)} \quad \underline{FeS} + (CaO) + C = \underline{Fe} + (CaS) + CO$$



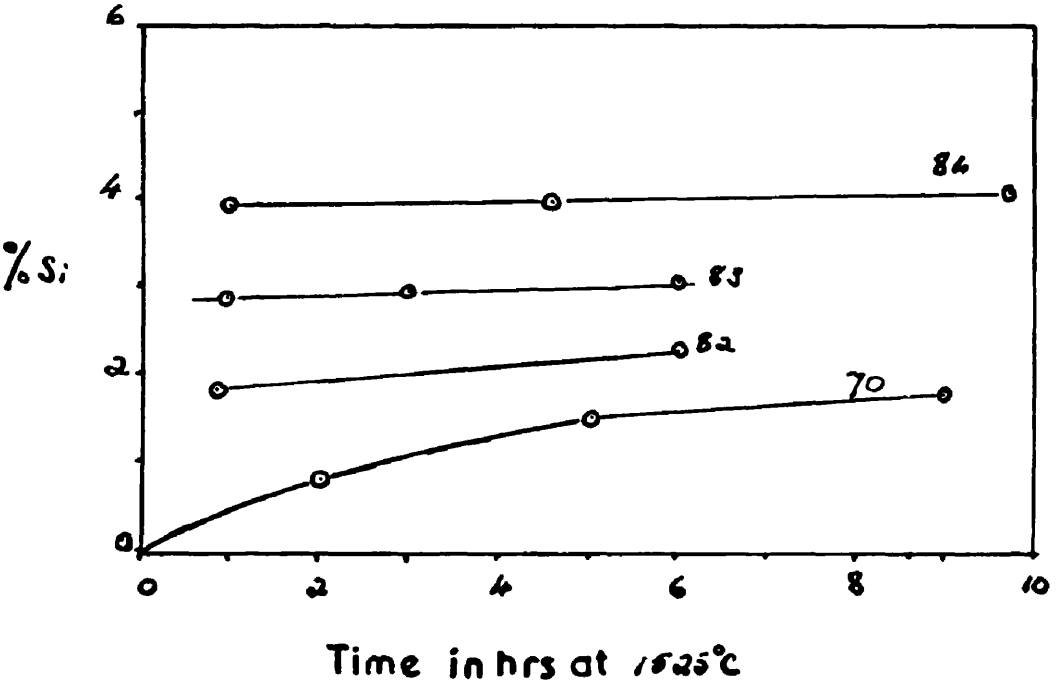


Fig. (32) Sulphur and silicon approach to equilibrium (Grant, Troiliand Chipman[8].)

can thus not come to equilibrium until the production of FeO by the reaction

$$(i) \quad (SiO_2) + \underline{2Fe} = \underline{Si} + 2(FeO)$$

has become slower than its removal by reaction (ii). This view is confirmed by the results of Grant, Troili, Chipman[8], Fig. (32). In experiment 70 in which no silicon was present in the slag initially the sulphur comes to equilibrium only slowly. When silicon has been added to the metal initially then the sulphur equilibrium is quickly attained, experiments 82, 83 and 84. The addition of silicon to the metal in amounts greater than approximately 1.5% slows down reaction (i) so that the FeO produced can be removed by reaction (ii). In the present work, because of the more acid slag, higher quantities of silicon must be present in the metal before the reduction of silicon from slag to metal is slowed down sufficiently for the FeO to come to equilibrium with carbon.

Hatch and Chipman[2] also found in their study of the sulphur equilibrium,

$$(vii) \quad \underline{FeS} + (CaO) + C = \underline{Fe} + (CaS) + CO$$

that, irrespective of whether FeS was added to the metal or CaS to the slag, the system finally approached equilibrium by transferring sulphur from metal to slag, i.e. when CaS was added to the slag more than the equilibrium sulphur content transferred initially to the metal. This fact can also be explained using reasoning similar to that used above. In the initial stages of the experiment the reduction of

silica is proceeding relatively rapidly so that FeO is present in the slag in excess of that in equilibrium with carbon. The reaction

$$(vi) \quad \underline{FeS} + (CaO) = (FeO) + (CaS)$$

is thus displaced to the left and more sulphur enters the metal than the quantity corresponding to the carbon oxygen potential. As the rate of silica reduction decreases the FeO content of the slag falls and the reaction then proceeds from left to right.

6. SUMMARY AND CONCLUSIONS.

The equilibrium positions at 1500°C of the following reactions have been studied

$$\text{(i)} \quad \underline{C} + (FeO) = \underline{Fe} + CO$$

$$\text{(ii)} \quad \underline{Si} + 2(FeO) = (SiO_2) + 2Fe$$

$$\text{(iii)} \quad (SiO_2) + 2C_{sol.} = \underline{Si} + 2CO$$

In order to determine the effect of varying amounts of FeO on the first two equilibria both temperature and the activity of silica were maintained constant. The lime silica ratio and the FeO content of the slags approximated to the values found in blast furnace slags but owing to experimental requirements the alumina content was much higher.

The interpretation of the results required that the activities of iron and carbon in iron-carbon-silicon solutions be known and a semi-empirical method was therefore developed by which these activities could be obtained. This method, analogous to that previously derived for the effect of two solutes on the activity of a third, gives values of the activity of carbon in good agreement with those calculated by an alternative method[13]. No direct confirmation of the activities of iron is available but the fact that the majority of the points representing the ternary solution in Fig. (18) lie below the line representing the values in the binary iron-carbon solution indicates that there is probably some small error in the method resulting in underestimated activities of iron.

Using the activity values so derived and the results obtained in the study of the above reactions the following conclusions have

been arrived at.

(i) The activity of FeO at low concentrations in a slag of the composition 31% CaO; 28% SiO_2; 41% Al_2O_3 exhibits strong negative deviations from ideal behaviour, values of $\gamma = \frac{a_{FeO}}{N_{FeO}}$ ranging from 0.13 at 0.3% FeO to 0.08 at 1.4% FeO. In view of the large effect of FeO on the silicon and sulphur distributions it would be desirable to know if this deviation occurs with more normal blast furnace type slags.

(ii) The FeO content of the slag has a large effect on the equilibrium silicon content of the underlying metal; the silicon content dropping from 5.5% to 0.2% for an increase in the slag FeO content of from 0.3 to 1.4%

(iii) New values of f^C_{Si}, the effect of carbon on the activity of silicon, have been obtained in the range 2.5 to 3.75%C. Above 3%C these values diverge widely from those obtained by Chipman[13] from the results of Körber.

The new values were obtained from the study of the reaction

$$\underline{Si} + 2(FeO) = (SiO_2) + \underline{2Fe}$$

in which it was found that the expression $K_{Si} = \frac{a_{Si} \times (\%FeO)^2}{a^2_{Fe}}$ exhibited large variations. By plotting K_{Si} against the percentage of silicon these variations were shown to be regular but could not be eliminated by replacing the percentages of FeO by the activities

determined from the study of reaction (i). The larger part of the variation, if not it all, was shown to be due to some error in the assessment of the activity of silicon. Using thermodynamic data to evaluate the ratio,

$$\frac{a_C^2}{a_{Si}} \times a_{SiO_2} = \frac{K_C^2}{K_{Si}}$$

inserting the value for the activity of silica found in the study of reaction (iii) and using the published values of f_{Si}^{Si} the new values of f_{Si}^{C} were calculated. Two curves of f_{Si}^{C} against percentage carbon were obtained depending on whether the values of f_{Si}^{Si} of Gokcen and Chipman[12] of those of Chipman[13] were used. Examination of the values of f_{Si}^{Si} revealed that those of Gokcen and Chipman are probably the more nearly correct and for this reason the values of f_{Si}^{C} calculated using these values of f_{Si}^{Si} are considered the more accurate. Because of this uncertainty in the values of f_{Si}^{Si} the values of f_{Si}^{C} will probably require amendment. However this is unlikely to affect the shape of the curve nor the divergence from the previously published values.

(iv) β silicon carbide was identified by means of x-rays as the material separating at 1500°C from iron containing 27% silicon and saturated with carbon. It is considered that the alloy in equilibrium at 1500°C with both graphite and silicon carbide contains approximately 23% silicon. By using the available thermodynamic

data on the formation of silicon carbide the activity of silicon in this alloy can be calculated. The value obtained is 0.076 on the pure scale or, by using the free energy of solution of silicon in iron calculated from the results of Gokcen and Chipman[12], 161 on the dilute solution scale. This value has been compared with previously determined activities of silicon (Fig. 30).

(v) The silicon content of metal in equilibrium at 1500°C with the slag of the composition 31% CaO, 28% SiO_2, 41% Al_2O_3 when the oxygen potential is controlled by the reaction,

$$2C + O_2 = 2CO$$

has been found to be 19%. The activity of silicon in this alloy has been calculated and from this together with the free energy expression for the reaction

$$(SiO_2) + 2C_{sol.} = \underline{Si} + 2CO$$

a value of 0.16 has been calculated for the activity of silica in the slag of the above composition.

(vi) When the reaction

$$(SiO_2) + 2C_{sol} = \underline{Si} + 2CO$$

is taking place in a slag-metal system contained in graphite crucibles, a higher than equilibrium content of FeO is maintained in the slags. For this reason it is considered that the above reaction

takes place in two steps, viz.

$$(i) \quad (SiO_2) + 2Fe = \underline{Si} + 2(FeO)$$

$$(ii) \quad 2(FeO) + 2C = \underline{2Fe} + 2CO$$

and that when far from equilibrium reaction (i) proceeds at a faster rate than does reaction (ii). This finding has been used to explain the results of Grant, Troili and Chipman[8] who found that the addition of silicon to the metal increased the rate at which sulphur transferred from metal to slag.

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APPENDIX.

In a recent paper, Gokcen and Chipman[1] have revised certain of their earlier findings[2]. In view of certain anomalies which they find in the reaction

$$2H_2 + \underline{O} = 2H_2O$$

they withdraw the activities of silicon which have been used throughout this work. This is added confirmation of what has already been found regarding these activity coefficients (p.76).

The authors also quote a new value for the free energy of formation of silica, viz.,

$$Si_{(liq)} + O_2 = SiO_2 \qquad \Delta G^\circ = -217,700 + 47.0T.$$

Two previously quoted expressions[3][4] gave values of ΔG° at 1500°C in substantial agreement but considerably higher than the value obtained from the above exxpression. It was therefore thought that until confirmation of the above expression is forthcoming that alteration of the conclusions arrived at in the present work was not justified. The following, however, summarises the principal alterations which the use of the above expression would make

(i) At 1600°C the free energy of solution of liquid silicon in iron to form the dilute solution of unit activity becomes -30,700 cals. i.e.

$$Si_{(liq)} = Si_{(in\ Fe)} \qquad \Delta G^\circ_{1600^\circ C} = -30,700 \text{ cals.}$$

This gives a ratio of activities on the two scales of measurement

of 0.00026 at 1600°C and, assuming the entropy term is small, 0.00017 at 1500°C.

(ii) The ratio,

$$\frac{a_C^2}{a_{Si}} = \frac{K_C^2}{K_{Si}} \times \frac{1}{a_{SiO_2}}$$

becomes equal to 3 instead of 8.5. Therefore, if the same assumptions are made as before regarding the validity of the values of f_{Si}^{Si} then the values of f_{Si}^{C} derived should be multiplied by $\frac{8.5}{3} = 2.8$. The derivation of accurate values of f_{Si}^{C} from the present results must however await the obtaining of accurate values of f_{Si}^{Si}.

(iii) The activity of silicon in equilibrium at 1500°C with both graphite and silicon carbide remains 0.076 on the pure scale but becomes approximately 450 on the dilute solution scale. This greatly increases the discrepancy between this value and the previously determined coefficients. (Fig. 30).

(iv) The activity of silica in the slag of the composition 31% CaO, 28% SiO_2, 41% Al_2O_3 would become 0.41 instead of 0.16.

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